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BORON NITRIDE AND SILICON NITRIDE SYSTEMS

.....Final Technical Report.....

by

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Abstract: (Approximately 75 words for Interim Report; 300 for Final)

A Compendium Of Boron Nitride and Silicon Nitride Phase Diagrams has been provided based on a critical assessment work of ternary systems: (Li,Na,K,Mg,Ca,Sr,Ba,Sc,Y,Tb,Ho,Dy,Er,Tm,Lu,U,Ti,Zr,Hf,V,Nb,Ta,Cr,Mo,W,Mn,Re,Fe,Co,Ni,Ru,Cu,Ag,Au,Zn,Cd,Al,In,Tl,Sn,Pb,Sb,Bi)-B-N and (Li,Be,Mg,Ca,Sr,Ba,Sc,Y,La,Ce,Sm,Ho,Ti,Zr,Hf,V,Nb,Ta,Cr,Mo,W,Mn,Re,Fe,Ru,Co,Rh,Ni,Cu,Ag,Au,Zn,Cd,Al,In,Tl,Sn,Pb,Sb,Bi)-Si-N including crystal data and thermodynamic data.

Key Words

Ternary systems: MetalBoronnitrides

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COMPENDIUM OF TERNARY PHASE DIAGRAMS OF  
METAL - BORON - NITROGEN and METAL - SILICON - NITROGEN SYSTEMS

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PART A TERNARY SYSTEMS M - B - N

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**PART A**

**Ternary Systems : Metal - Boron - Nitrogen**



## **PART A TERNARY SYSTEMS M - B - N**

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## SYSTEM BORON - LITHIUM - NITROGEN (B-Li-N)

### INTRODUCTION / EXPERIMENTAL

Information on phase equilibria and compound formation in the Li-B-N system is due to [59Gou, 60Wen, 61Wen, 66Kud, 69DeV, 72Dev, 86Yam] and [8 Yam], which all agree on the existence of a ternary compound  $\text{Li}_3\text{BN}_2$  with several pressure modifications (see Table 1). Heating powder compacts of  $\text{Li}_3\text{N} + \text{BN}$  in a Mo-boat in a stream of nitrogen between 650 to 700°C was claimed as optimal conditions to obtain  $\text{Li}_3\text{BN}_2$  [59Gou, 69DeV], the reaction being strongly exothermic [69DeV]. Melting of  $\text{Li}_3\text{BN}_2$  was reported at 870±5°C [59Gou].

Based on earlier preliminary data by [60Wen, 61Wen], the p-T diagram of  $\text{Li}_3\text{BN}_2$  (Fig.1) was investigated over the pressure and temperature range from 1.0 to 6.5 GPa and 300 to 1900°C employing optical and X-ray powder diffraction analysis [69DeV, 72DeV]. All experiments were done in pyrophyllite-Ta cells in a belt apparatus where pressure was applied to a given value and then the temperature was raised at a rate of 400K/min; temperature and pressure were held at 10 to 15 min followed by quenching in ~ 30 sec with the pressure still applied.

### BINARY SYSTEMS

No equilibrium diagram is available for the Li-B system; however, a series of lithium borides exist, which are listed in Table 1. For details see [84Mair, 89Ok, 90Mas]. At 1450°C  $\text{Li}_3\text{B}_{14}$  was found in equilibrium with  $\beta$ -boron [84Mail]; a result, which casts doubts on the existence of phases such as  $\text{LiB}_{12}$  or  $\text{LiB}_{10}$  and rather suggests an extended solubility of Li in boron. There is practically no solubility of B in Li.

Phase equilibria in the Li-Li<sub>3</sub>N subsystem are given in [90Mas] revealing  $\text{Li}_3\text{N}$  as the only stable phase; crystallographic data of  $\text{Li}_3\text{N}$  and of the azide  $\text{LiN}_3$  are listed in Table 1. Interstitial solubility of N in Li is very low.

## SOLID PHASES / ISOTHERMAL SECTIONS

Agreement exists on the structural modification of  $\text{Li}_3\text{BN}_2$  obtained under  $10^5\text{Pa}$  when quenched from the reaction temperature [59Gou, 69DeV, 86Yam]. Slow cooling of a mixture  $\text{Li}_3\text{N} + 1.0$  to  $1.2$  BN, which was first heated to  $900^\circ\text{C}$ , kept at temperature for 7h and cooled to  $700^\circ\text{C}$  at a rate of  $1.5$  to  $3$  K/h in a stream of nitrogen, resulted, however, in a modification [86Yam] different from the one first reported by [59Gou] (see Table 1).

Fig.1 reveals the formation of two high pressure forms of  $\text{Li}_3\text{BN}_2$ ;  $\text{Li}_3\text{BN}_2$  (I) was recognized to be identical with the phase labelled "complex" by [60Wen, 61Wen]. Reversibility of the transition  $\text{Li}_3\text{BN}_2 - \text{Li}_3\text{BN}_2$  (I) was not established when held at  $550^\circ\text{C}$ ,  $5.5$  GPa for 30 min, whereas partial conversion was seen when  $\text{Li}_3\text{BN}_2$  (I) was heated at  $700^\circ\text{C}$  in  $10^5$  Pa of  $\text{N}_2$  for 5h. As it proved unquenchable [69DeV], a layerlike structure was suggested for  $\text{Li}_3\text{BN}_2$  (II) from optical, mechanical and thermal properties.

The section  $\text{Li}_3\text{BN}_2 - \text{BN}$  has been investigated by [72DeV] at  $5.0$  GPa and was reported to be pseudobinary revealing a eutectic  $l \Rightarrow \text{Li}_3\text{BN}_2 + \text{cBN}$  at  $6$  mol %BN at  $1610 \pm 25^\circ\text{C}$  (Fig.2). As the upper limit of the  $l + \text{cBN}$  field was observed at  $1450 \pm 25^\circ\text{C}$ , a possible crystal growth region for cBN is only  $140^\circ\text{C}$ , however, the corresponding liquidus is unfavourably steep. At  $1550^\circ\text{C}$  a ternary reaction involving cBN,  $\text{Li}_3\text{BN}_2$  (I), a boron containing phase plus liquid was observed; this temperature is lower than the first appearance of melt in the  $\text{Li}_3\text{BN}_2 - \text{BN}$  section ( $1610^\circ\text{C}$ ) and corresponds to the lower limit of cBN formation from the reaction  $\text{Li} + \text{BN}$  [66Kud]. A comparison of the favourable pressure temperature conditions for the production of cBN using  $\text{Li}_3\text{N}$ ,  $\text{Mg}_3\text{N}_2$  or  $\text{Ca}_3\text{N}_2$ , is shown in Fig.3.

## MISCELLANEOUS

Infrared spectra of the quenched form of  $\text{Li}_3\text{BN}_2$  were interpreted in terms of  $[\text{N}=\text{B}=\text{N}]^{2-}$  molecular ions; nearly linear  $[\text{N}=\text{B}=\text{N}]^{2-}$  groups with B-N double bonds were observed for slowly cooled  $\text{Li}_3\text{BN}_2$  [86Yam].

Li-ion conductivity of a polycrystalline sample of slowly cooled  $\text{Li}_3\text{BN}_2$  was  $4.10^{-5} \text{ Sm}^{-1}$  at  $125^\circ\text{C}$  with an activation energy of  $64 \text{ kJ/mol}$  [85Yam].

## REFERENCES

- [60Wen] R.H.Wentorf, Jr., US-Patent 2947617, 2.Aug.1960, as quoted by [69DeV]
- [61Wen] R.H.Wentorf, Jr., "Synthesis of the Cubic Form of Boron Nitride", J.Chem.Phys. 34 (1961) 809-812
- [61Gou] J.Goubeau and W.Anselment, "On Ternary Metal Boron Nitrides" (in German), Z.Anorg.Allg.Chemie 310 (1961) 248-260
- [66Kud] K.Kudaka, H.Konno and T.Matoba, Kogyo Kagaku Zasshi (J.Chem.Soc.Japan, Ind.Chem.Section) 69 (1966) 365
- [69DeV] R.C.DeVries and J.F.Fleischer, "The System  $\text{Li}_3\text{BN}_2$  at High Pressures and Temperatures", Mater.Res.Bull. 4 (1969) 433-442
- [72DeV] R.C.DeVries and J.F.Fleischer, "Phase Equilibria Pertinent to the Growth of Cubic Boron Nitride", J.Crystal Growth 13/14 (1972) 88-92
- [84Mai] G.Mair, "The Lithium-Boron System" (in German), Thesis, Univ. Stuttgart, (1984) pp 99
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc. Met., Metals Park, Oh, 1985)
- [85Yam] H.Yamane, S.Kikkawa and M.Koizumi, Solid State Ionics 15 (1985) 31
- [86Yam] H.Yamane, S.Kikkawa, H.Horiuchi and M.Koizumi, "Structural Polymorph of Lithium Boron Nitride  $\text{Li}_3\text{BN}_2$ ", J.Solid State Chem. 65 (1986) 6-12
- [88Yam] H.Yamane  $\text{Li}_3\text{BN}_2$  (I)
- [89Oka] H.Okamoto, "The B-Li System", Bull.Alloy Phase Diagrams 10 (1989) 230-232
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met.Intl., Metals Park, Oh, 1990)

Table 1: Solid phases in the system B-Li-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\beta$ -Li 180.5- -193°	cI2 Im $\bar{3}$ m W	a= 350.93	[90Mas]
$\alpha$ -Li <-193°	hP2 P6 $_3$ /mmc Mg	a= 311.1 c= 509.3	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
$\alpha$ -rhB <1200°	hR36 R $\bar{3}$ m $\alpha$ -B	a= 490.9 c=1258.2	[85Vil]
LiB $_{12}$	tP*	a=1016 c=1428	[890ka]
LiB $_6$	LiB $_{12}$ -		[890ka]
Li $_8$ B $_{14}$	tI136 I $\bar{4}$ 2d Li $_8$ B $_{14}$	a=1076.4 c= 894.7	[84Mai] $\rho_x=2.214 \text{ Mg m}^{-3}$
LiB $_4$	c** -	a= 720	[890ka]
Li $_8$ B $_{10}$	hP25 P6/mmm Li $_8$ B $_{10}$	a= 823.3 c= 415.6	[84Mai] $\rho_x=1.706 \text{ Mg m}^{-3}$
LiB $_9$	tP16 P4/mbm Li $_8$ B $_9$ (CaB $_9$ -deriv.)	a= 597.8 c= 418.8	[84Mai]
LiB $_8$	- -	-	[890ka]

LiB	t**	a=1391	[890ka]
	-	c= 815	
Li <sub>5</sub> B <sub>6</sub>	hR10	a= 493	[890ka] or Li <sub>7</sub> B <sub>6</sub>
	R <sub>3</sub> m or I <sub>4</sub> 3m		
	Li <sub>5</sub> B <sub>6</sub>		
Li <sub>5</sub> B	c**		[890ka]
Li <sub>5</sub> N	hP4	a= 364.8	[85Vil]
815°	P6/mmm	c= 387.5	
	Li <sub>5</sub> N		
LiN <sub>5</sub>	mC8	a= 562.7	[85Vil]
	C2/m	b= 331.9	
		c= 497.9	
		$\beta$ = 107.4°	
BN <sub>hex</sub>	hP*	a= 250.4	[85Vil]
	P6 <sub>3</sub> /mmc	c= 666.1	
	BN <sub>hex</sub>		
* Li <sub>5</sub> BN <sub>2</sub>	-	-	[59Gou] at 10 <sup>5</sup> Pa, quench
<870°	Li <sub>5</sub> AlN <sub>2</sub>		$\rho_{exp}$ =1.755 Mgm <sup>-3</sup>
* Li <sub>5</sub> BN <sub>2</sub>	mF24	a= 515.02	[86Yam] at 10 <sup>5</sup> Pa, slow c
	P2 <sub>1</sub> /c	b= 708.24	$\rho_{exp}$ =1.74 Mgm <sup>-3</sup>
	Li <sub>5</sub> BN <sub>2</sub>	c= 679.08	
		$\beta$ = 112.956°	
* Li <sub>5</sub> BN <sub>2</sub> (I)	-	-	[61Wen, 69DeV]
>0.7 GPa	-		
* Li <sub>5</sub> BN <sub>2</sub> (II)	-	-	[61Wen, 69DeV]
>2.5 GPa			

Fig.1: The P - T diagram for  $\text{Li}_3\text{BN}_2$  (after [72DeV])

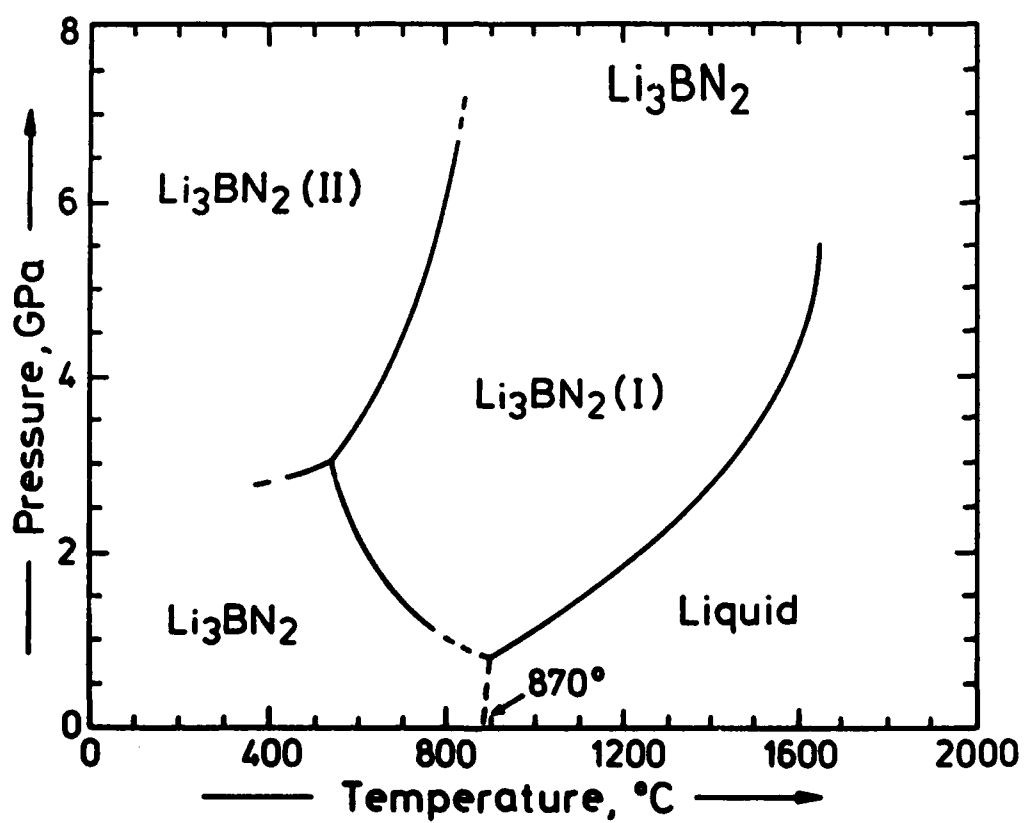




Fig.2. The pseudobinary section  $\text{Li}_3\text{BN}_2$  - BN at 5 GPa (after [72DeV])

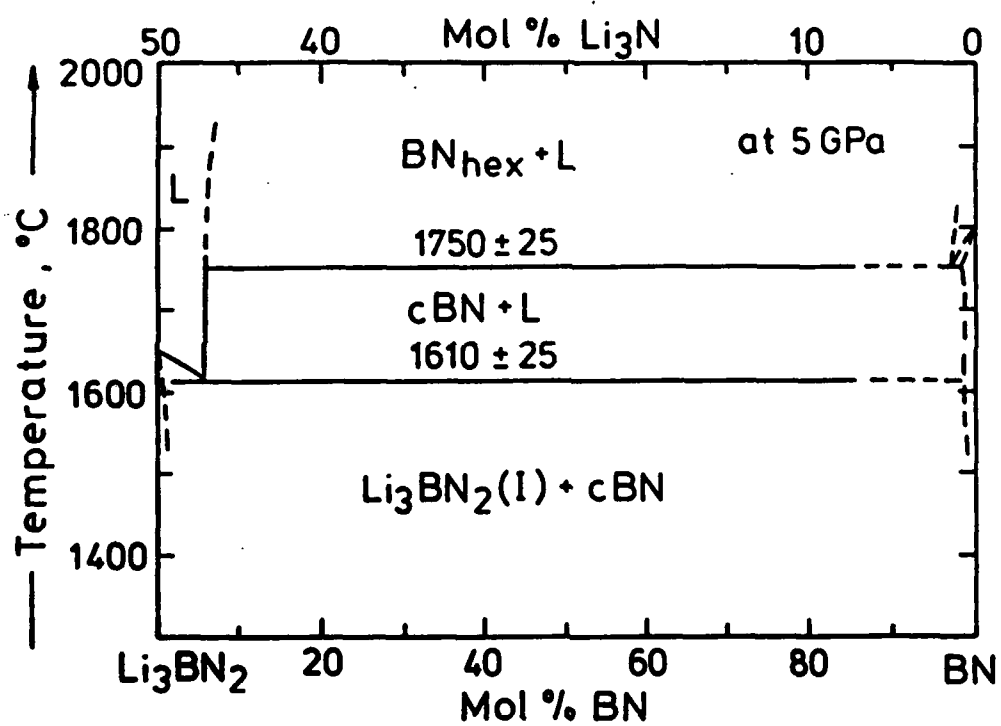
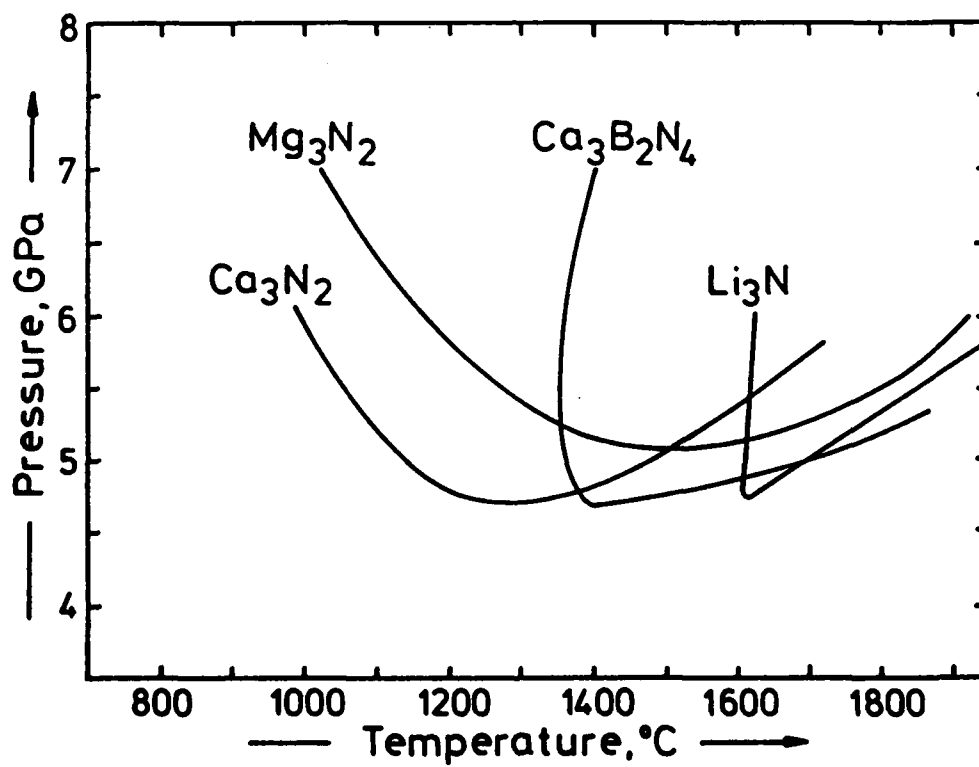


Fig.3. Comparison of the stability region for cBN using various catalysts.



## SYSTEM BORON - SODIUM - NITROGEN (B-Na-N)

### INTRODUCTION / EXPERIMENTAL

A black powder was obtained when sodium was heated with BN in sealed quartz capillaries at 400°C for 24h; after washing in ethanol the product was dark grey revealing new low angle X-ray peaks which were believed to correspond to intercalation; the formula  $\text{NaBN}_{1.8}$  was obtained from chemical analysis [69Fre].

Hexagonal boron nitride was converted to cBN with sodium at 1750°C and 9.3 GPa [60Wen].

### REFERENCES

- [60Wen] R.H.Wentorf, Jr., "Abrasive Material and Preparation Thereof",  
US Patent 2947617 GEC, 2.Aug. (1960)
- [69Fre] A.G.Freeman and J.P.Larkindale, "Evidence for the Formation of  
Boron Nitride-Alkali Metal Intercalation Compounds", Inorg.  
Nucl. Chem. Lett. 5 (1969) 937-939

Table 1: Solid phases in the system B-Na-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\beta$ -Na 97.86- -233°	cI2 $Im\bar{3}m$ W	a= 429.06	[90Mas]
$\alpha$ -Na <-233°C	hP2 $P6_3/mmc$ Mg	a= 376.7 c= 615.4	[90Mas]
$\beta$ -rhB <2092°	hR111 $R\bar{3}m$ $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
$\alpha$ -rhB <1200°	hR36 $R\bar{3}m$ $\alpha$ -B	a= 490.9 c=1258.2	[85Vil]
BN <sub>hex</sub>	hP* $P6_3/mmc$ BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]
* NaBN <sub>18</sub>	- BN <sub>hex</sub> -intercalation	-	[69Fre]

## SYSTEM BORON - POTASSIUM - NITROGEN (B-K-N)

### INTRODUCTION / EXPERIMENTAL

A black powder was obtained when potassium was heated with BN in sealed quartz capillaries at 300°C for 24h; after washing in ethanol the product was dark grey revealing new low angle X-ray peaks which were believed to correspond to intercalation; the formula  $\text{KBN}_{1.9}$  was obtained from chemical analysis [69Fre].

Hexagonal boron nitride was converted to cBN with potassium at 1700°C and 9.5 GPa [60Wen].

No reaction was observed when potassiumamide and Bn were heated in sealed iron containers up to 1200°C [61Gou].

### REFERENCES

- [60Wen] R.H.Wentorf, Jr., "Abrasive Material and Preparation Thereof",  
US Patent 2947617 GEC, 2. August (1960)
- [69Fre] A.G.Freeman and J.P.Larkindale, "Evidence for the Formation of  
Boron Nitride-Alkali Metal Intercalation Compounds", Inorg.  
Nucl. Chem. Lett. 5 (1969) 937-939

Table 1: Solid phases in the system B-K-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
K <63.71°C	cI2 Im $\bar{3}$ m W	a= 532.1	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vi1] [85Vi1]
$\alpha$ -rhB <1200°	hR36 R $\bar{3}$ m $\alpha$ -B	a= 490.9 c=1258.2	[85Vi1]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vi1]
* KBN <sub>13</sub>	- BN <sub>hex</sub> -intercalation	-	[69Fre]

## SYSTEM BORON - MAGNESIUM - NITROGEN (B-Mg-N)

### INTRODUCTION / EXPERIMENTAL

Information on phase equilibria and compound formation in the Mg-B-N system is due to [66Kud, 72Dev, 79End1, 79End2, 81Sat, 81Ely, 89Pik, 89Shi] and [89Hoh], which all agree on the existence of a ternary compound  $Mg_3BN_4$  for which two modifications have been observed [81Ely, 89Pik, 89Hoh] (see Table 1).

Based on preliminary high pressure data by [60Wen, 66Kud, 67Fil] defining the minimum temperature for the formation of cBN at  $\sim 1700^\circ C$  in the presence of magnesiumborides, phase relations along the join Mg -  $Mg_3B_2N_4$  - BN have been investigated at 2.5 GPa in the temperature range from 800 to  $1600^\circ C$  employing DTA-, optical and X-ray powder diffraction analysis supported by conventional quenching techniques [79End1, 79End2, 81End] (see Fig.1). The experiments were done in pyrophyllite-Ta cells in a belt apparatus where pressure was applied to a given value and then the temperature was raised at a rate of 200 to 250 K/min; temperature and pressure were held for 20 min followed by quenching in  $\sim 30$  sec with the pressure still applied. No reaction was found between Mg and BN below  $1100^\circ C$ , whereas above  $1150^\circ C$  yellow lath-like plates of  $Mg_3B_2N_4$  and magnesiumborides  $MgB_2$ ,  $MgB_{\sim 6}$ ,  $MgB_{\sim 12}$  were formed [79End1]. The precipitation of hBN from the eutectic liquid was observed for temperatures higher than  $1300^\circ C$ .

### BINARY SYSTEMS

A tentative equilibrium diagram for the Mg-B system is given in [90Mas], revealing the formation of three stable magnesium borides, which are listed in Table 1. There is practically no mutual solid solubility of B, Mg.

No phase diagram is available for the Mg-N system. For  $Mg_3N_2$  only the  $\alpha$ -modification has been reported [65Ell] (see Table 1). Interstitial solubility of N in Mg is very low.

## SOLID PHASES / ISOTHERMAL SECTIONS

In a cursory p-T diagram of the system  $\text{Mg}_3\text{N}_2$  - BN [81Ely] showed the ranges of existence of two modifications of  $\alpha\text{-Mg}_3\text{B}_2\text{N}_4$  (1000 to 1450°C, > 2 GPa),  $\beta\text{-Mg}_3\text{B}_2\text{N}_4$  (> 1600°C, 3.5 to 6 GPa) with an intermediate two-phase region in between. The X-ray powder pattern as reported by [79End1] for  $\text{Mg}_3\text{B}_2\text{N}_4$  was claimed to essentially correspond to this two-phase region  $\alpha+\beta\text{-Mg}_3\text{B}_2\text{N}_4$  [81Ely]. The existence of two modifications of  $\text{Mg}_3\text{B}_2\text{N}_4$ , however, is not confirmed by [89Hoh].

At 2.5 GPa  $\text{Mg}_3\text{B}_2\text{N}_4$  was reported to melt at 1489±5°C [79End1] and at 1685±10°C at 6.5 GPa [89Hoh].

Fig.1 reveals the phase relations in two subsystems Mg -  $\text{Mg}_3\text{B}_2\text{N}_4$  and  $\text{Mg}_3\text{B}_2\text{N}_4$  - BN which at 2.5 GPa were shown to be of a simple eutectic type [79End1].  $l = \text{Mg}_3\text{B}_2\text{N}_4 + \text{hBN}$  is at 1295±7°C, 2.5 GPa [79End1] and at 1380±10°C at 6.5 GPa [89Hoh].

The p-T regions of cBN in the systems Mg-BN and  $\text{Mg}_3\text{N}_2$ -BN were investigated up to 8 GPa and 2300°C [79End2, 81Sat]. In the Mg-BN system pressure and temperature necessary for the formation of cBN were found to decrease with increasing oxygen content of the starting hBN material [79End2]; the lower limit of the cBN region for hBN with 1.9 mass%O is ~1380°C at 6 to 8 GPa, but 1700°C at 6 GPa for hBN with 7.9 mass%O. In the  $\text{Mg}_3\text{N}_2$  system oxygen had little effect on the lower limits of pressure and temperature, cBN-yields, however, decreased with oxygen contents [81Sat].

Coexistence of  $\text{Mg}_3\text{B}_2\text{N}_4$  and  $\text{Mg}_3\text{BN}_3$  was observed within the low-temperature cBN region [89Pik, 89Hoh].

A comparison of the favourable pressure temperature conditions for the production of cBN using  $\text{Li}_3\text{N}$ ,  $\text{Mg}_3\text{N}_2$  or  $\text{Ca}_3\text{N}_2$ , is shown in Fig.3 of the section Li-B-N.

## MISCELLANEOUS

Infrared spectra of  $\text{Mg}_3\text{B}_2\text{N}_4$  formed at 2.5 GPa were interpreted in terms of  $[\text{N}=\text{B}=\text{N}]^{2-}$  molecular ions [79End1].  $\text{Mg}_3\text{B}_2\text{N}_4$  slowly decomposes in moist environment, at higher temperatures it easily oxidizes to  $\text{Mg}_3(\text{BO}_3)_2$  [79End1].



The influence of P on the crystallization kinetics of cBN in the  $\text{MgB}_2$ -BN system has been studied by [89Shi] at 5 GPa and 1570 to 1800°C; 0.1 to 0.5 mass% P considerably increase the nucleation rate and reduce the nucleation energy.

#### REFERENCES

- [60Wen] R.H.Wentorf, Jr., "Abrasive Material and Preparation Thereof" US-Patent 2947617 GEC, 2.Aug.1960
- [66Kud] K.Kudaka, H.Konno and T.Matoba, Kogyo Kagaku Zasshi (J.Chem.Soc.Japan,Ind.Chem.Section) 69 (1966) 365
- [67Fil] N.E.Filonenko, V.I.Ivanov, L.I.Feld'gun, M.I.Sokhor and L.F.Vereshchagin, "Magnesium Borides Prepared under Superhigh Pressure Conditions", Sov.Phys.Dokl. 12 (1968) 833-835, translated from Dokl.Acad.Nauk SSSR 175 (1967) 1266-1269
- [72DeV] R.C.DeVries and J.F.Fleischer, "Phase Equilibria Pertinent to the Growth of Cubic Boron Nitride", J.Crystal Growth 13/14 (1972) 88-92
- [79End1] T.Endo, O.Fukunaga and M.Iwata, "Precipitation Mechanism of BN in the Ternary System of B-Mg-N", J.Mater.Sci. 14 (1979) 1676-1680
- [79End2] T.Endo, O.Fukunaga and M.Iwata, "Growth Pressure-Temperature Region of Cubic BN in the System BN-Mg", J.Mater.Sci. 14 (1979) 1375-1380
- [81Ely] V.P.Elyutin, N.I.Polushin, K.P.Burdina, V.P.Polyakov, Ya.A.Kalashnikov, K.N.Semenenko and Yu.A.Pavlov, "Interaction in the System  $\text{Mg}_3\text{N}_2$ -BN", Dokl.Acad.Nauk SSSR, 259 (1981) 112-6
- [81Sat] T.Sato, H.Hiraoaka, T.Endo, O.Fukunaga and M.Iwata, "Effect of Oxygen on the Growth of Cubic Boron Nitride using  $\text{Mg}_3\text{N}_2$  as Catalyst", J.Mater. Sci. 16 (1981) 1829-1834
- [85Vil] C.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc. Met., Metals Park, Oh, 1985)
- [89Pik] S.N.Pikalov, N.V.Tarisenko, O.A.Sobokary and K.A.Bondarevich, Poroshkov.Metall. (3) (1989) 71-74

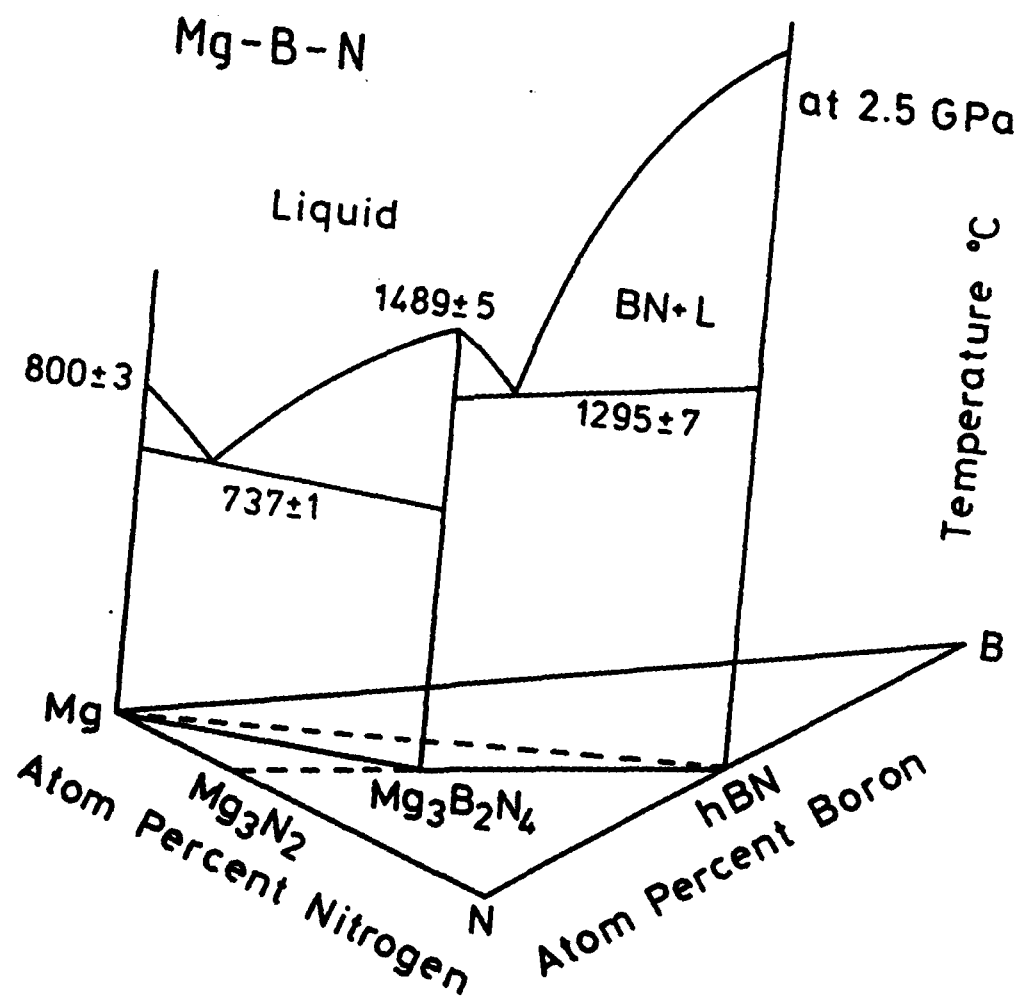
- [89Shi] V.B.Shipilo and L.M.Gameza, "Crystallization of Sphalerite -Type Boron Nitride in the BN-MgB<sub>2</sub>-P System", Translated from Izv. Akad Nauk SSSR, Neorg. Mater. 25 (1989) 51-55
- [89Hoh] C.Hohfeld, "Peculiarities of the Cubic Boron Nitride Formation in the System BN-Mg<sub>3</sub>N<sub>2</sub>", J.Mater.Sci.Lett. 8 (1989) 1082-1084
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met.Intl., Metals Park, Oh, 1990)

Table 1: Solid phases in the system B-Mg-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Mg 650°	hP2 P6 <sub>3</sub> /mmc Mg	a= 320.94 c= 521.07	[90Mas]
β-rhB <2092°	hR111 R $\bar{3}$ m β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
α-rhB <1200°	hR36 R $\bar{3}$ m α-B	a= 490.9 c=1258.2	[85Vil]
MgB <sub>7</sub> <2300°	oI64 Imma MgB <sub>7</sub>	a= 597.0 b=1048.0 c= 812.5	[85Vil]
MgB <sub>4</sub> <1850°	oP20 Pnma MgB <sub>4</sub>	a= 546.4 b= 442.8	[85Vil]
MgB <sub>2</sub> <1550°	hP3 P6/mmm AlB <sub>2</sub>	a= 308.4 c= 352.2	[85Vil]
α-Mg <sub>3</sub> N <sub>2</sub> <550°	cI80 Ia $\bar{3}$ Mn <sub>2</sub> O <sub>3</sub>	a= 996.4	[85Vil]

BN <sub>hex</sub>	hP*	a= 250.4	[85Vil]
	P6 <sub>3</sub> /mmc	c= 666.1	
	BN <sub>hex</sub>		
* $\alpha$ -Mg <sub>3</sub> B <sub>2</sub> N <sub>4</sub>	-	-	[81Ely]
>2 GPa			
* $\beta$ -Mg <sub>3</sub> B <sub>2</sub> N <sub>4</sub>	-	-	[81Ely]
>3.5-6 GPa			
* Mg <sub>3</sub> BN <sub>2</sub>	-	-	[89Hoh] at 6.5 GPa

Fig.1: The partial system Mg-B-N (after [79End1])



## SYSTEM BORON - CALCIUM - NITROGEN (B-Ca-N)

### INTRODUCTION / EXPERIMENTAL

Information on phase equilibria and compound formation in the Ca-B-N system is due to [60Wen, 61Gou, 72Dev, 81End] and [83Sat], which all agree on the existence of a ternary compound  $\text{Ca}_3\text{B}_2\text{N}_4$  (see Table 1).

Heating powder compacts of  $\text{Ca}_3\text{N}_2 + \text{BN}$  in a Mo-boat in a stream of nitrogen between 800 to 1150°C was claimed as optimal conditions to obtain  $\text{Ca}_3\text{B}_2\text{N}_4$  [61Gou, 72Dev]. The reaction was said to be incomplete after 3h at 800°C. Melting of  $\text{Ca}_3\text{B}_2\text{N}_4$  was reported at 1412±3°C [81End].

Based on preliminary high pressure data by [60Wen] defining the minimum temperature for the formation of cBN at ~1300°C and 6.9GPa, phase relations along the join Ca -  $\text{Ca}_3\text{B}_2\text{N}_4$  - BN have been investigated at 2.5 GPa in the temperature range from 800 to 1600°C employing DTA-, optical and X-ray powder diffraction analysis supported by conventional quenching techniques [81End, 83Sat] (see Fig.1). The experiments were done in pyrophyllite/Ta cells in a belt apparatus where pressure was applied to a given value and then the temperature was raised at a rate of 200 to 250K/min; temperature and pressure were held for 20 min followed by quenching in ~ 30 sec with the pressure still applied. Above 1150°C,  $\text{Ca}_3\text{B}_2\text{N}_4$  was formed together with small amounts of  $\text{Ca}_3\text{N}_2$  and  $\text{CaB}_6$  [81End]. The low temperature limit of the precipitation of cBN from the  $\text{Ca}_3\text{B}_2\text{N}_4$ -melt was found to be closely related to the  $\text{Ca}_3\text{B}_2\text{N}_4 + \text{BN}$  eutectic at 1316 ± 6°C [81End]. [83Sat] studied the nucleation and growth mechanism of cBN crystals.

### BINARY SYSTEMS

A tentative equilibrium diagram for the Ca-B system is suggested in [90Mas], revealing the formation of only one stable calcium boride,  $\text{CaB}_6$ , despite there seem to be no doubts about the existence of  $\text{CaB}_4$  [61Joh], (see Table 1). There is practically no mutual solid solubility of B, Ca.

Informations on the Ca-N phase diagram are still unsatisfactory; a critical assessment is due to [90Itk]. Crystallographic data are listed in Table 1. Interstitial solubility of N in Ca is very low.

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 reveals the phase relations in two subsystems  $\text{Ca} - \text{Ca}_3\text{B}_2\text{N}_4$  and  $\text{Ca}_3\text{B}_2\text{N}_4 - \text{BN}$  which at 2.5 GPa were shown to be of a simple eutectic type [B1End].  $l \rightleftharpoons \text{Ca}_3\text{B}_2\text{N}_4 + \text{hBN}$  is at  $1316\pm 6^\circ\text{C}$ , 2.5 GPa and  $l \rightleftharpoons \text{Ca} + \text{Ca}_3\text{B}_2\text{N}_4$  is at  $1032\pm 5^\circ\text{C}$  at 2.5 GPa [B1End]. At 2.5 GPa  $\text{Ca}_3\text{B}_2\text{N}_4$  was reported to melt at  $1412\pm 3^\circ\text{C}$  [B1End].

The p-T regions of cBN in the systems  $\text{Ca}-\text{BN}$  and  $\text{Ca}_3\text{B}_2\text{N}_4-\text{BN}$  were investigated up to 6.5 GPa and  $1800^\circ\text{C}$  [B1End, B3Sat] and found to be practically identical. According to the composition-temperature diagram of the  $\text{Ca}_3\text{B}_2\text{N}_4-\text{BN}$  system at 5.4 GPa ( see Fig.2 ), the growth of cBN was governed by the solubility difference of hBN and cBN in liquid  $\text{Ca}_3\text{B}_2\text{N}_4$ -flux [B3Sat].

A comparison of the favourable pressure temperature conditions for the production of cBN using  $\text{Li}_3\text{N}$ ,  $\text{Mg}_3\text{N}_2$  or  $\text{Ca}_3\text{B}_2\text{N}_4$ , is shown in Fig.3 of the section Li-B-N.

## MISCELLANEOUS

Infrared spectra of  $\text{Ca}_3\text{B}_2\text{N}_4$  formed at 2.5 GPa were interpreted in terms of  $[\text{N}=\text{B}=\text{N}]^{3-}$  molecular ions [61Gou].  $\text{Ca}_3\text{B}_2\text{N}_4$  slowly decomposes in moist environment, at higher temperatures it easily oxidizes to  $\text{Ca}(\text{BO})_2$ .

## REFERENCES

- [60Wen] R.H.Wentorf, Jr., "Abrasive Material and Preparation Thereof", US-Patent 2947617, 2.Aug.1960,
- [61Gou] J.Goubeau and W.Anselment, "On Ternary Metal Boron Nitrides" (in German), Z.Anorg.Allg.Chemie 310 (1961) 248-260
- [68Lau] Y.Laurent, "Contribution to the Study of the Systems Calcium-Nitrogen and Calcium-Silicon-Nitrogen", Rev.Chim.Minér. 5 (1968) 1019-1050
- [72DeV] R.C.DeVries and J.F.Fleischer, "Phase Equilibria Pertinent to the Growth of Cubic Boron Nitride", J.Crystal Growth 13/14 (1972) 88-92
- [81End] T.Endo, O.Fukunga and M.Iwata, "The Synthesis of cBN using  $\text{Ca}_9\text{B}_2\text{N}_4$ ", J.Mater.Sci.16 (1981) 2227-2232
- [83Sat] T.Sato, T.Endo, S.Kashima, O.Fukunaga and M.Iwata, "Formation Mechanism of cBN Crystals under Isothermal Conditions in the System BN- $\text{Ca}_9\text{B}_2\text{N}_4$ ", J.Mater.Sci. 18 (1983) 3054-3062
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc. Met., Metals Park, Oh, 1985)
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met.Intl., Metals Park, Oh, 1990)
- [90Itk] V.P.Itkin and C.B.Alcock, "The Ca-N System", Bull. Alloy Phase Diagrams 11 (1990) 497-503

Table 1: Solid phases in the system B-Ca-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\beta$ -Ca 842-443°C	cI2 Im $\bar{3}$ m W	a= 448.0	[90Mas]
$\alpha$ -Ca <443°C	cF4 Fm $\bar{3}$ m Cu	a= 558.84	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vi1] [85Vi1]
$\alpha$ -rhB <1200°	hR36 R $\bar{3}$ m $\alpha$ -B	a= 490.9 c=1258.2	[85Vi1]
CaB <sub>4</sub> <°	tP20 P4/mbm UB <sub>4</sub>	a= 711 c= 411	[61Joh]
CaB <sub>6</sub> <2500°C	cF7 Pm $\bar{3}$ m CaB <sub>6</sub>	a= 414.5	[85Vi1]
Ca <sub>2</sub> N	hR3 R $\bar{3}$ m Sm m**	a= 363.8 c=1878  a= 753.5 b= 363.8 c= 629.9 $\beta$ = 123.85°	[85Vi1] stabil. by H <sub>2</sub> ? [68Lau]
$\alpha$ -Ca <sub>3</sub> N <sub>2</sub>	cI80 Ia $\bar{3}$ Mn <sub>2</sub> O <sub>3</sub>	a=1147.3	[85Vi1]
$\gamma$ -Ca <sub>3</sub> N <sub>2</sub>	o*40	a=1782 b=1156 c= 358	[85Vi1] metastable?



$\text{Ca}_3\text{N}_2$ (I)	o**	a= 562.5 b=1114. c=1361.	[90Itk] at 4.6 GPa
$\text{Ca}_{11}\text{N}_8$	tP38 $P4_2/mnm$	a=1445 c= 360	[85Vil]
$\text{CaN}_6$	$\text{Ca}_{11}\text{N}_8$ oF56 Fddd	a=1132 b=1107 c= 595	[85Vil]
$\text{BN}_{\text{hex}}$	hP* $P6_3/mmc$ $\text{BN}_{\text{hex}}$	a= 250.4 c= 666.1	[85Vil]
* $\text{Ca}_3\text{B}_2\text{N}_4$ <1412°C at 2.5 GPa	-	-	[61Gou] $\rho_{\text{exp}} = 2.86 \text{ Mg m}^{-3}$

Fig.1: The partial system Ca-B-N (after [B1End])

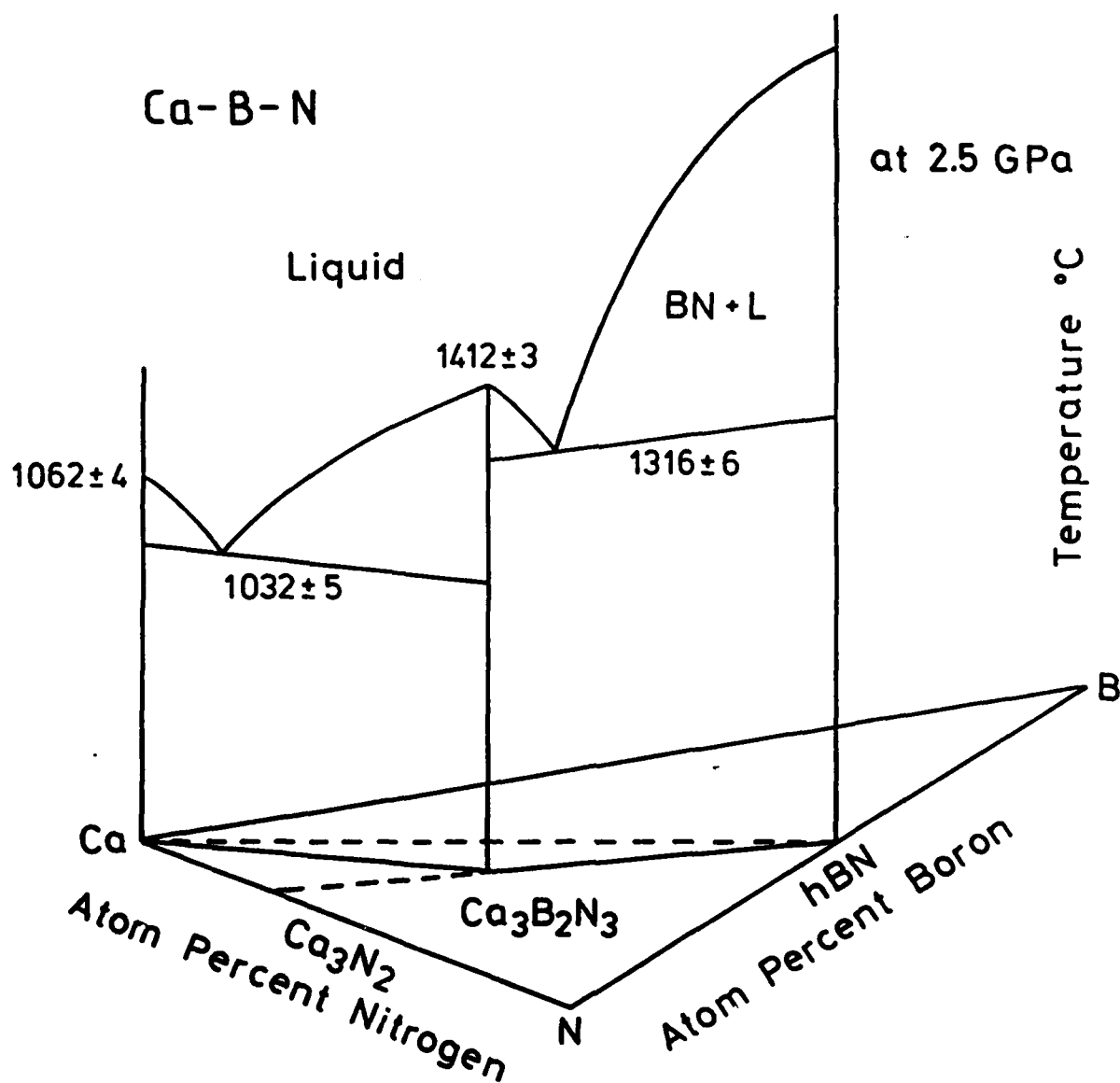
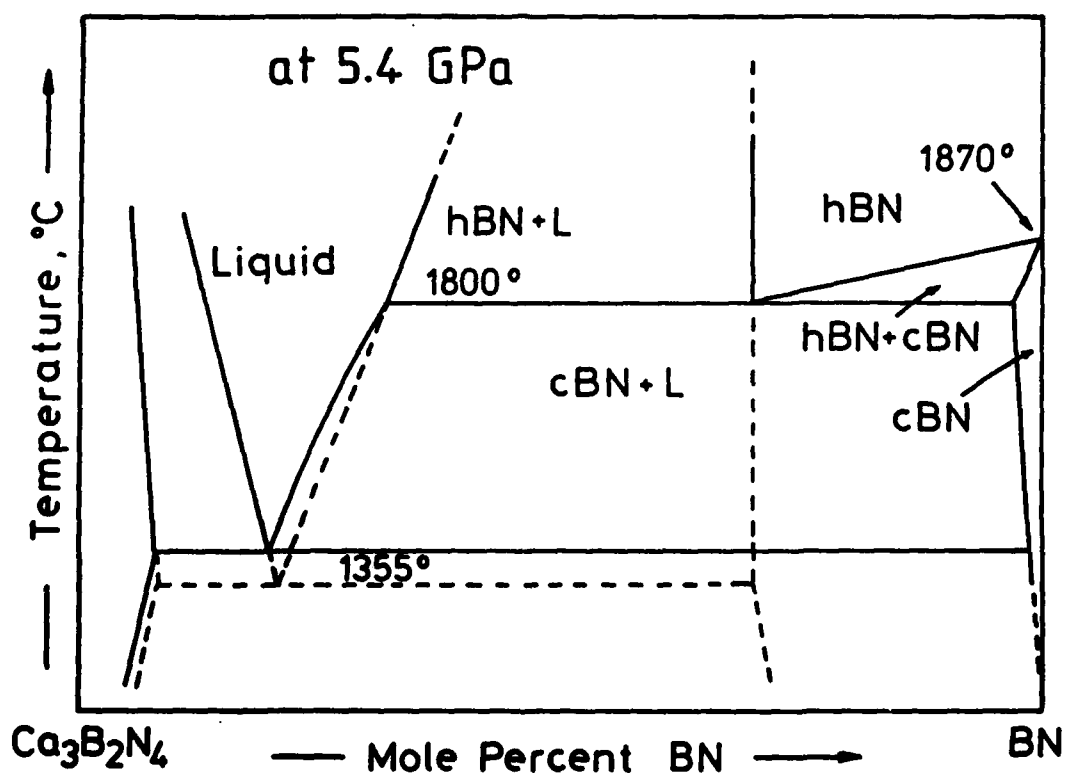


Fig.2: Phase equilibria in the section  $\text{Ca}_3\text{B}_2\text{N}_8$  - BN at 5.4 GPa  
( after [83Sat])



## SYSTEM BORON - STRONTIUM - NITROGEN (B-Sr-N)

### INTRODUCTION / EXPERIMENTAL

No phase diagram Sr-B-N exists; information on phase relations and compound formation is due to [74Gau] who reported on the existence of a ternary compound  $\text{Sr}_3\text{B}_2\text{N}_4$  from X-ray analysis of samples reacted at 900°C for 30 h (see Table 1).

Preliminary high pressure experiments by [60Wen] reported the formation of cBN from hBN at 8.7 GPa and ~1600°C using Sr-metal as a catalyst.

### BINARY SYSTEMS

A tentative equilibrium diagram for the Sr-B system is given in [90Mas], revealing the formation of one stable strontium boride,  $\text{SrB}_6$ , (see Table 1). There is practically no mutual solid solubility of B, Sr.

No phase diagram is available for the Sr-N system. Crystallographic data are listed in Table 1. Interstitial solubility of N in Sr is very low.

### SOLID PHASES / ISOTHERMAL SECTIONS

The X-ray powder pattern as reported by [74Gau] for  $\text{Sr}_3\text{B}_2\text{N}_4$  was claimed to essentially correspond to the one of  $\text{Ca}_3\text{B}_2\text{N}_4$  (isotypic?).

### MISCELLANEOUS

Infrared spectra of  $\text{Sr}_3\text{B}_2\text{N}_4$  were interpreted in terms of  $[\text{N}=\text{B}=\text{N}]^{3-}$  molecular ions [74Gau].  $\text{Sr}_3\text{B}_2\text{N}_4$  slowly decomposes in moist environment, at higher temperatures it easily oxidizes to  $\text{Sr}_3(\text{BO}_3)_2$  [74Gau].

## REFERENCES

- [60Wen] R.H.Wentorf, Jr., "Abrasive Material and Preparation Thereof"  
US-Patent 2947617 GEC, 2.Aug.1960
- [70Gau] J.Gaude and J.Lang, "The System Strontium-Nitrogen", Rev.Chim.  
Minerale 7 (1970) 1059-1067
- [74Gau] J.Gaude and J.Lang, "The System Strontium-Nitrogen, VI. On  
the Boron Nitride of Strontium and its Transformation  
into Orthoborate", Rev.Chim. Minerale 11 (1974) 80-84
- [85Vil] C.Villars and L.D.Calvert, "Pearsons Handbook of  
Crystallographic Data for Intermetallic Phases" (Amer.Soc.  
Met., Metals Park, Oh, 1985)
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed.,  
(Amer.Soc.Met.Intl., Metals Park, Oh, 1990)

Table 1: Solid phases in the system B-Sr-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\beta$ -Sr 769-547°	cI2 Im $\bar{3}$ m W	a= 487	[90Mas]
$\alpha$ -Sr <547°C	cF4 Fm $\bar{3}$ m Cu	a= 608.4	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m	a=1092.51 c=2381.43	[85Vi1] [85Vi1]
$\alpha$ -rhB <1200°	$\beta$ -B hR36 R $\bar{3}$ m	a= 490.9 c=1258.2	[85Vi1]
SrB <sub>6</sub> <2500°C	$\alpha$ -B cP7 Fm $\bar{3}$ m	a= 419.84	[85Vi1]
Sr <sub>2</sub> N	CaB <sub>6</sub> hR3 R $\bar{3}$ m Sm m**	a= 724.6 $\alpha$ = 30.8° a= 719 b= 385 c= 665 $\beta$ = 108°	[85Vi1] [70Gau]
Sr <sub>3</sub> N <sub>2</sub> <1030°	hP*		[85Vi1]
SrN <sub>6</sub>	Ba <sub>3</sub> N <sub>2</sub> oF56 Fddd	a=1180.88 b=1153.43 c=611.62	[85Vi1]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vi1]
* Sr <sub>3</sub> B <sub>2</sub> N <sub>4</sub>	-	-	[74Gau] $\rho_{exp}$ =3.72Mgm <sup>-3</sup>

## SYSTEM BORON - BARIUM - NITROGEN (B-Ba-N)

### INTRODUCTION / EXPERIMENTAL

No phase diagram Ba-B-N exists; information on phase relations and compound formation is due to [61Gou] who reported on the existence of a ternary compound  $Ba_3B_2N_4$  from X-ray analysis of powder compacts of  $Ba_3N_2 + BN$  which have been reacted in a sealed quartz capillary for 3 h at 700 to 900°C (see Table 1).

Preliminary high pressure experiments by [60Wen] reported the formation of cBN from hBN at 8.0 to 8.7 GPa and ~1600 to 1700°C using Ba-metal as a catalyst.

### BINARY SYSTEMS

A tentative equilibrium diagram for the Ba-B system is given in [90Mas], revealing the formation of one stable barium boride,  $BaB_6$ , (see Table 1). There is practically no mutual solid solubility of B, Ba.

No phase diagram is available for the Ba-N system. Crystallographic data are listed in Table 1. Interstitial solubility of N in Ba is very low.

### SOLID PHASES / ISOTHERMAL SECTIONS

The X-ray powder pattern as reported by [61Gou] for  $Ba_3B_2N_4$  was claimed to essentially correspond to the one of  $Ba_3B_2N_4$  (isotypic?).

### MISCELLANEOUS

Infrared spectra of  $Ba_3B_2N_4$  were interpreted in terms of  $[N=B=N]^{2-}$  molecular ions [61Gou].  $Ba_3B_2N_4$  slowly decomposes in moist environment, at higher temperatures it easily oxidizes to  $Ba_3(BO_3)_2$  [61Gou].

## REFERENCES

- [60Wen] R.H.Wentorf, Jr., "Abrasive Material and Preparation Thereof"  
US-Patent 2947617 GEC, 2.Aug.1960
- [61Gou] J.Goubeau and W.Anselment, "On Ternary Metal-Boron Nitrides",  
(in German) Z.Anorg.Allg.Chemie 310 (1961) 28-260
- [85Vil] C.Villars and L.D.Calvert, "Pearsons Handbook of  
Crystallographic Data for Intermetallic Phases" (Amer.Soc.  
Met., Metals Park, Oh, 1985)
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed.,  
(Amer.Soc.Met.Intl., Metals Park, Oh, 1990)



Table 1: Solid phases in the system B-Ba-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Ba <727°	cI2 Im $\bar{3}$ m W	a= 501.3	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
$\alpha$ -rhB <1200°	hR36 R $\bar{3}$ m $\alpha$ -B	a= 490.9 c=1258.2	[85Vil]
BaB <sub>6</sub> <2500°C	cP7 Pm $\bar{3}$ m CaB <sub>6</sub>	a= 426.8	[85Vil]
Ba <sub>9</sub> N <sub>2</sub>	hP*	a= 522	[85Vil]
BaN <sub>6</sub>	Ba <sub>9</sub> N <sub>2</sub> mP14 P2 <sub>1</sub> /m BaN <sub>6</sub>	c= 550 a= 959 b= 439 c= 542 $\beta$ =99.7°	[85Vil]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]
* Ba <sub>9</sub> B <sub>2</sub> N <sub>4</sub>	-	-	[61Gou]

## INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Sc-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20 $\mu$ m in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N<sub>2</sub>) usually consisted of a primary reaction at 1200°C for 90h followed by a final reaction at 1400°C for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O<sub>2</sub> and < 4 ppm H<sub>2</sub>O. Starting materials were ingots of 3N-Sc, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [91Kle].

## BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Sc system revealed consistency with the data available in [76Spe], [84Vil] and [90Mas]; see Table 1. A critical assessment is due to [90Spe]. The solubility of B in Sc is negligible [90Spe]; the maximum solubility of Sc in  $\beta$ -B is close to ScB<sub>2</sub> [78Cal].

No equilibrium diagram exists for the N-Sc system and solid solubility of N in Sc is said to be small; a comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure ScN is the only stable nitride [72Kie] (Table 1).

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at  $1400^{\circ}\text{C}$  under 1 bar of argon (in the absence of external nitrogen pressure) [91Kle]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium  $\text{ScN} + \text{ScB}_2 + \text{BN}$ . Thus there is no compatibility between (Sc) and BN. As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Sc in BN at  $1400^{\circ}\text{C}$ , and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91Kle].

No signs of compound formation at higher nitrogen contents were observed [91Kle] from heat treatments under 1 bar of  $\text{N}_2$  at  $1400^{\circ}\text{C}$  (100h) and at  $1800^{\circ}\text{C}$  (20h) respectively : in both cases the limiting tie line reported was  $\text{ScN} + \text{BN} + \text{N}_2$ .

## THERMODYNAMICS

A thermodynamic modelling of the binary system Sc-B is due to [90Spe]; see Table 2.

## REFERENCES

- [72Kie] R.Kieffer, P. Ettmayer and S. Pajakoff, "On The Mononitrides and on Nitrogen-rich Nitrides of the Rare Earths, 1<sup>st</sup> Commun.", (in German), Monatsh. Chemie 103 (1972) 1285-1298
- [76Spe] K. E. Spear, "Phase Behavior and Related Properties of Rare Earth Borides", in "Phase Diagrams in Materials Science and Technology", Ed. A.M. Alper, (Acad. Press, NY), 1976, 91-159
- [78Cal] B.Callmer, "A Single Crystal Diffractometry Investigation of Scandium in  $\beta$ -rh. Boron", J.Solid State Chem. 23 (1978) 391-98
- [78Fro] E. Fromm, H. Jehn and G. Hoerz, "Gases and Carbon in Metals" ZAED, Physics Data, 5-3 (1978) pp 2
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, Oh, 1985)
- [89Rem] K. Remschnig and P.Rogl, "The Ternary Systems: Rare Earth - Aluminium-Boron, RE=Sc,Y,La,Ce,Pr,Nd,Gd,Tb,Dy,Ho,Er and Tm", Proceedings of the 12<sup>th</sup> Plansee Seminar, Eds. H.Bildstein and H. Ortner, ( Tyrolia Verlag, Innsbruck,Austria ), Vol II, (1989) 599-607
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams" 2<sup>nd</sup> Ed., (Amer.Soc.Met.Intl., Metals Park,Oh, 1990)
- [90Spe] K.E.Spear and P.K.Liao, "The B-Sc System", Bull. Alloy Phase Diagrams 11 (1990) 321-324
- [91Kle] H. Klesnar and P.Rogl, "Phase Relations in The Ternary Systems Rare Earth (RE) - Boron - Nitrogen, RE=Tb through Lu and Sc,Y", High Temperatures-High Pressures, (1991) in press

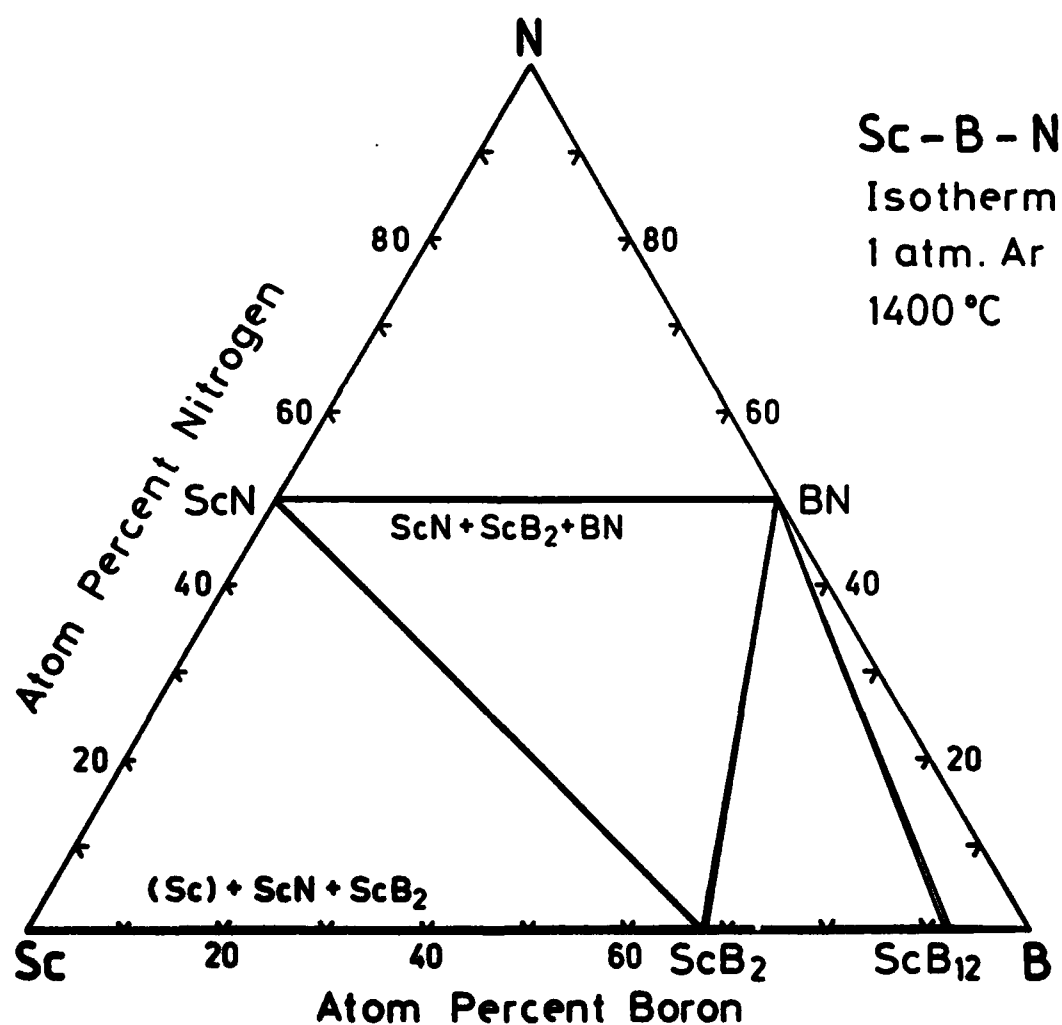
Table 1: Solid phases at 1400°C in the systems B - Sc - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\beta$ -Sc 1541-1337°	cI2 Im $\bar{3}m$ W	a= 454.1	[90Mas]
$\alpha$ -Sc <1337°	hP2 P6 $_3$ /mmc Mg	a= 330.88 c= 526.80	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}m$ $\beta$ -B	a=1092.51 c=2381.43	[78Cal]
		a=1096.58 c=2408.75	[78Cal] for ScB <sub>20</sub>
ScB <sub>2</sub> <2250°	hP3 P6/mmm AlB <sub>2</sub>	a= 314.8 c= 351.6	[85Vil]
ScB <sub>12</sub> <2040°	tI26 I4/mmm ScB <sub>12</sub>	a= 523.47 c= 735.83	[78Cal]
ScN	cF8 Fm $\bar{3}m$ NaCl	a= 450.5	[85Vil]
BN <sub>hex</sub>	hP4 P6 $_3$ /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]

Table 2: Thermodynamic data for the system Sc-B (after [90Spe])

Phase	$\Delta_f G$ ( J/gramatom )	Ref.
1.0000 Sc	$\Delta_{fus} G(\text{Sc}) = 18110 - 10.275 T$	[90Spe]
1.0000 B	$\Delta_{fus} G(\text{B}) = 50210 - 21.23 T$	
1.0000 $\alpha\text{Sc}$	$\Delta_f G(\alpha\text{Sc}) = 0$	
1.0000 $\beta\text{Sc}$	$\Delta_f G(\beta\text{Sc}) = 4010 - 2.495 T$	
0.3333 $\text{ScB}_2$	$\Delta_f G(\text{ScB}_2) = -102330 + 5.0 T$	
0.0769 $\text{ScB}_{12}$	$\Delta_f G(\text{ScB}_{12}) = -36980 + 2.0 T$	
1.0000 $\beta\text{B}$	$\Delta_f G(\beta\text{B}) = 0$	
Liquid	$\Delta G^{ex} = x(1-x)\{-177050 - 34.9 T + (-3335 + 68.9 T)(1-2x)\}$	

Fig.1: Isothermal section of the system B - Sc -N at 1400°C under 1 bar of argon ( in the absense of external nitrogen ).



## SYSTEM BORON - YTTRIUM - NITROGEN (B-Y-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Y-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than  $20\mu\text{m}$  in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N<sub>2</sub>) usually consisted of a primary reaction at  $1200^{\circ}\text{C}$  for 90h followed by a final reaction at  $1400^{\circ}\text{C}$  for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O<sub>2</sub> and  $< 4$  ppm H<sub>2</sub>O. Starting materials were ingots of 3N-Y, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at  $1400^{\circ}\text{C}$ . Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [91Kle].

### BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Y system revealed consistency with the data available in [76Spe], [84Vil] and [90Mas]; see Table 1.

A tentative equilibrium diagram for the yttrium-rich region of the system N-Y is given by [74Car]; the solid solubility of N in Y was claimed to be 3 at% N at the temperature of the peritectoid formation of  $\alpha\text{-Y}$  from  $\beta\text{-Y} + \text{YN}$  ( $1490^{\circ}$ ) [74Car]. A comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure YN is the only stable nitride (see Table 1); at higher nitrogen



pressure  $Y_2N_{2.8-x}$  with the  $Mn_2O_3$ -type ( $cI80 - Ia\bar{3}$ ) has been reported [72Kie].

#### SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at  $1400^\circ C$  under 1 bar of argon (in the absence of external nitrogen pressure) [91Kle]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium  $YN + YB_4 + BN$ . Thus there is no compatibility between (Y) and BN. As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Y in BN at  $1400^\circ C$ , and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91Kle].

No signs of compound formation at higher nitrogen contents were observed [91Kle] from heat treatments under 1 bar of  $N_2$  at  $1400^\circ C$  (100h) and at  $1800^\circ C$  (20h) respectively : in both cases the limiting tie line reported was  $YN + BN$ .

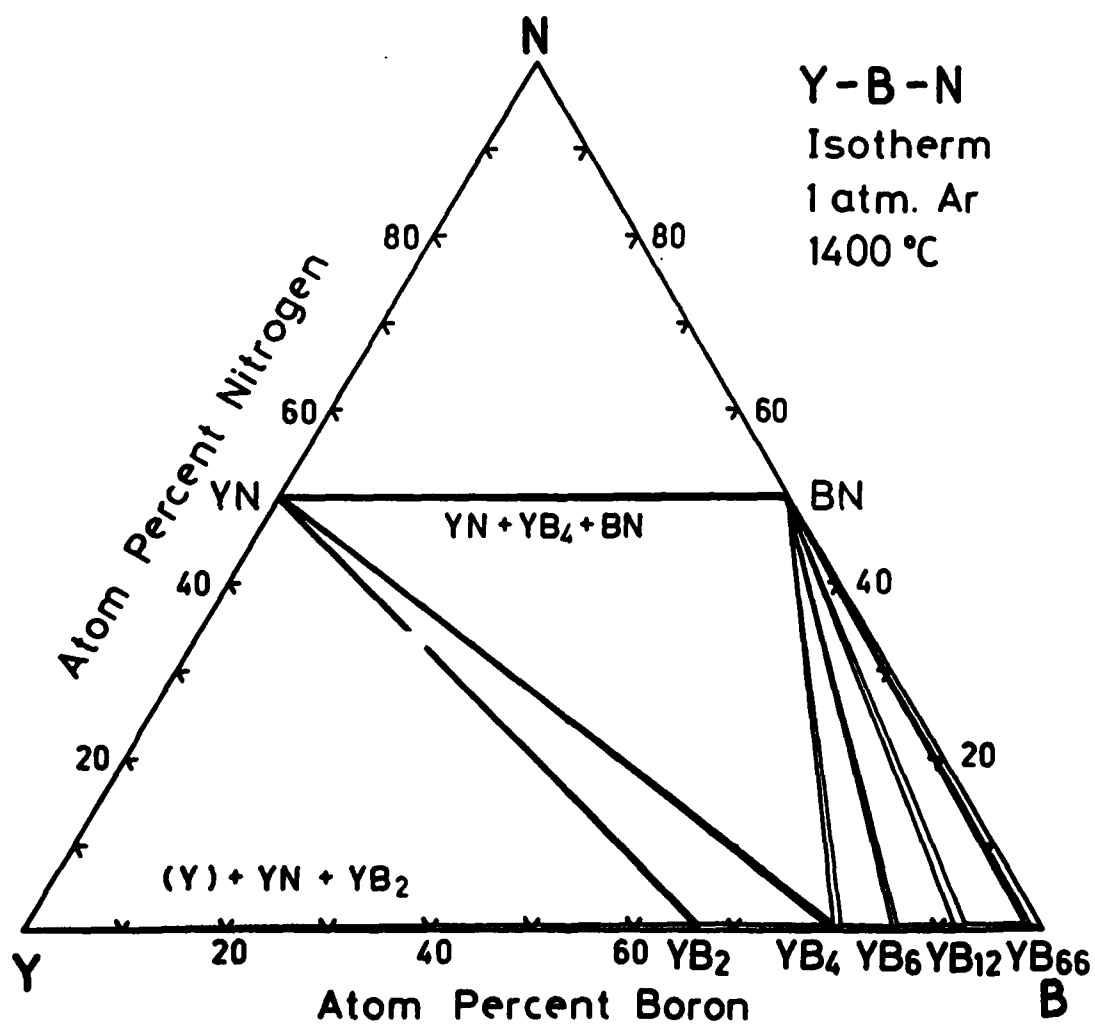
## REFERENCES

- [72Kie] R.Kieffer, P. Ettmayer and S. Pajakoff, "On The Mononitrides and on Nitrogen-rich Nitrides of the Rare Earths, 1<sup>st</sup> Commun." (in German), Monatsh. Chemie 103 (1972) 1285-1298
- [74Car] O. N. Carlson, R. R. Lichtenberg and J. C. Warner, "Solid Solubilities of Oxygen, Carbon and Nitrogen in Yttrium", J Less-Comm. Met. 35 (1974) 275-284
- [76Spe] K. E. Spear, "Phase Behavior and Related Properties of Rare Earth Borides", in "Phase Diagrams in Materials Science and Technology", Ed. A.M.Alper, (Acad. Press, NY, 1976) 91-159
- [78Fro] E. Fromm, H. Jehn and G. Hoerz, "Gases and Carbon in Metals" ZAED, Physics Data, 5-3 (1978) pp 2
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, Oh, 1985)
- [89Rem] K. Remschnig and P.Rogl, "The Ternary Systems: Rare Earth - Aluminium - Boron, RE=Y,La,Ce,Pr,Nd,Gd,Tb,Dy,Ho,Er and Tm", Proceedings of the 12<sup>th</sup> Plansee Seminar, Eds. H.Bildstein and H. Ortner, ( Tyrolia Verlag, Innsbruck,Austria ), Vol II, (1989) 599-607
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams" 2<sup>nd</sup> Ed., (Amer.Soc.Met.Intl., Metals Park,Oh, 1990)
- [91Kle] H. Klesnar and P.Rogl, "Phase Relations in The Ternary Systems Rare Earth (RE)-Boron-Nitrogen, RE=Tb through Lu and Sc,Y", High Temperatures-High Pressures, (1991) submitted for publication

Table 1: Solid phases at 1400°C in the system B-Y-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\alpha$ -Y <1478°	hP2 P6 <sub>3</sub> /mmc Mg	a= 364.82 c= 573.18	[86Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vi1] [85Vi1]
YB <sub>2</sub> <2100°	hP3 P6/mmm AlB <sub>2</sub>	a= 328.9 c= 384.3	[85Vi1]
YB <sub>4</sub> <2800°	tP20 P4/mbm ThB <sub>4</sub>	a= 711.1 c= 401.7	[85Vi1]
YB <sub>6</sub> <2600°	cP7 Pm $\bar{3}$ m CaB <sub>6</sub>	a= 412.8	[85Vi1]
YB <sub>12</sub> <2200°	cF52 Fm $\bar{3}$ m UB <sub>12</sub>	a= 746	[85Vi1]
YB <sub>66</sub> <2100°	cF1608 Fm $\bar{3}$ c YB <sub>66</sub>	a=2344	[85Vi1]
YN	cF8 Fm $\bar{3}$ m NaCl	a= 487.8	[85Vi1]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vi1]

Fig.1: Isothermal section of the system B - Y -N at 1400°C under 1 bar of argon ( in the absense of external nitrogen ).



## SYSTEM BORON- TERBIUM- NITROGEN (B-Tb-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Tb-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than  $20\mu\text{m}$  in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace ( under 1 bar of 5N-Ar or 5N-N<sub>2</sub> ) usually consisted of a primary reaction at  $1200^{\circ}\text{C}$  for 90h followed by a final reaction at  $1400^{\circ}\text{C}$  for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O<sub>2</sub> and  $< 4$  ppm H<sub>2</sub>O. Starting materials were ingots of 3N-Tb, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at  $1400^{\circ}\text{C}$ . Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [90Kle].

### BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Tb system revealed consistency with the data available in [76Spe, 90Lia] and [90Mas]; see Table 1. Mutual solid solubilities are expected to be negligible.

No equilibrium diagram exists for the N-Tb system and solid solubility of N in Tb is said to be small; a comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure TbN is the only stable nitride (see Table 1); at higher nitrogen pressure Tb<sub>2</sub>N<sub>3-x</sub> with the Mn<sub>2</sub>O<sub>3</sub>-type (c180 - Ia $\bar{3}$ , a=1066 pm ) has been reported [72Kie].

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at  $1400^{\circ}\text{C}$  under 1 bar of argon (in the absence of external nitrogen pressure) [91Kle]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium  $\text{TbN} + \text{TbB}_4 + \text{BN}$ . Thus there is no compatibility between (Tb) and BN. As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Tb in BN at  $1400^{\circ}\text{C}$ , and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91Kle].

No signs of compound formation at higher nitrogen contents were observed [91Kle] from heat treatments under 1 bar of  $\text{N}_2$  at  $1400^{\circ}\text{C}$  (100h) and at  $1800^{\circ}\text{C}$  (20h) respectively : in both cases the limiting tie line reported was  $\text{TbN} + \text{BN}$ .

## REFERENCES

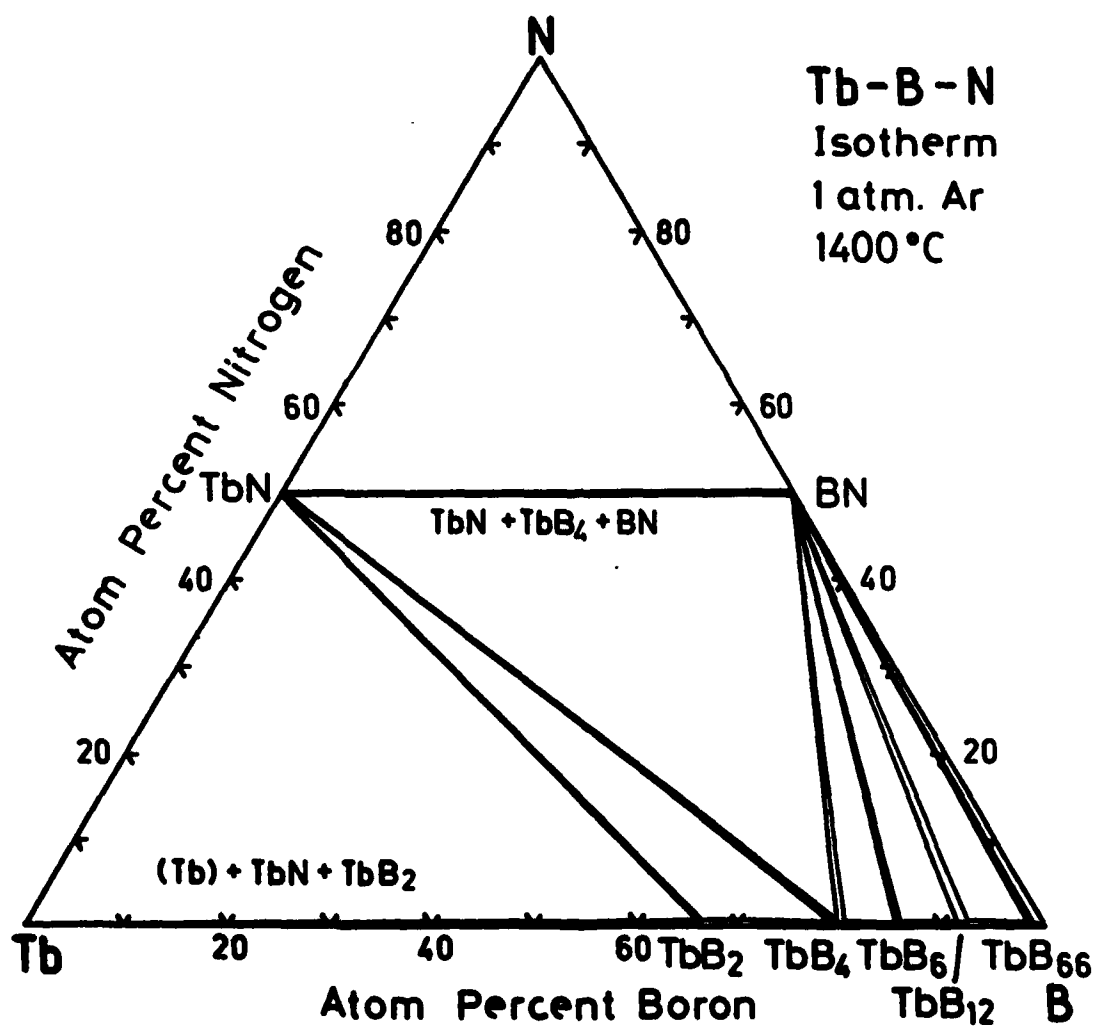
- [72Kie] R.Kieffer, P. Ettmayer and S. Pajakoff, "On The Mononitrides and on Nitrogen-rich Nitrides of the Rare Earths, 1<sup>st</sup> Commun.", (in German), Monatsh. Chemie 103 (1972) 1285-1298
- [76Spe] K. E. Spear, "Phase Behavior and Related Properties of Rare Earth Borides", in "Phase Diagrams in Materials Science and Technology", Ed. A.M.Alper, (Acad. Press, NY, 1976) 91-159
- [78Fro] E. Fromm, H. Jehn and G. Hoerz, "Gases and Carbon in Metals" ZAED, Physics Data,5-3 (1978) pp 2
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met.,Metals Park, Oh, 1985)
- [89Rem] K. Remschnig and P.Rogl, "The Ternary Systems: Rare Earth - Aluminium - Boron, RE=Y,La,Ce,Pr,Nd,Gd,Tb,Dy,Ho,Er and Tm", Proceedings of the 12<sup>th</sup> Plansee Seminar, Eds. H.Bildstein and H. Ortner, ( Tyrolia Verlag, Innsbruck,Austria ), Vol II, (1989) 599-607
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met.Intl., Metals Park,Oh, 1990)
- [90Lia] P.K.Liao and K.E.Spear, "The B-Tb System", Bull.Alloy Phase Diagrams 11 (1990) 325-328
- [91Kle] H. Klesnar and P.Rogl, "Phase Relations in The Ternary Systems Rare Earth (RE)-Boron-Nitrogen, RE=Tb through Lu and Sc,Y", High Temperatures-High Pressures, (1991) in press

Table 1: Solid phases at 1400°C in the system B-Tb-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\beta$ -Tb 1356-1289°	cI2 Im $\bar{3}m$ W	a= 402	[86Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}m$ $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
TbB <sub>2</sub> <2100°	hP3 P6/mmm AlB <sub>2</sub>	a= 329.0 c= 387.8	[85Vil]
TbB <sub>4</sub> <2600°	tP20 P4/mbm ThB <sub>4</sub>	a= 712.0 c= 404.2	[85Vil]
TbB <sub>6</sub> <2340°	cP7 Pm $\bar{3}m$ CaB <sub>6</sub>	a= 410.0	[85Vil]
TbB <sub>12</sub> <2200°	cF52 Fm $\bar{3}m$ UB <sub>12</sub>	a= 750.7	[85Vil]
TbB <sub>∞</sub> <2100°	cF160B Fm $\bar{3}c$ YB <sub>∞</sub>	a=2345.7	[85Vil]
TbN	cF8 Fm $\bar{3}m$ NaCl	a= 493.6	[85Vil]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]



Fig.1: Isothermal section of the system B - Tb -N at 1400°C under 1 bar of argon ( in the absence of external nitrogen ).



## SYSTEM BORON- DYSPROSIUM- NITROGEN (B-Dy-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Dy-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than  $20\mu\text{m}$  in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace ( under 1 bar of 5N-Ar or 5N-N<sub>2</sub> ) usually consisted of a primary reaction at  $1200^{\circ}\text{C}$  for 90h followed by a final reaction at  $1400^{\circ}\text{C}$  for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O<sub>2</sub> and  $< 4$  ppm H<sub>2</sub>O. Starting materials were ingots of 3N-Dy, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at  $1400^{\circ}\text{C}$ . Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [91Kle].

### BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Dy system revealed consistency with the data available in [76Spe], [84Vil] and [90Mas]: see Table 1. Mutual solid solubilities are expected to be negligible.

No equilibrium diagram exists for the N-Dy system and solid solubility of N in Dy is said to be small; a comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure DyN is the only stable nitride (see Table 1); at higher nitrogen pressure Dy<sub>2</sub>N<sub>3-x</sub> with the Mn<sub>2</sub>O<sub>3</sub>-type (c180 - Ia $\bar{3}$ ,  $a=1058$  pm ) has been reported [72Kie].

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at  $1400^{\circ}\text{C}$  under 1 bar of argon (in the absence of external nitrogen pressure) [91K1e]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium  $\text{DyN} + \text{DyB}_4 + \text{BN}$ . Thus there is no compatibility between (Dy) and BN. As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Dy in BN at  $1400^{\circ}\text{C}$ , and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91K1e].

No signs of compound formation at higher nitrogen contents were observed [91K1e] from heat treatments under 1 bar of  $\text{N}_2$  at  $1400^{\circ}\text{C}$  (100h) and at  $1800^{\circ}\text{C}$  (20h) respectively : in both cases the limiting tie line reported was  $\text{DyN} + \text{BN}$ .

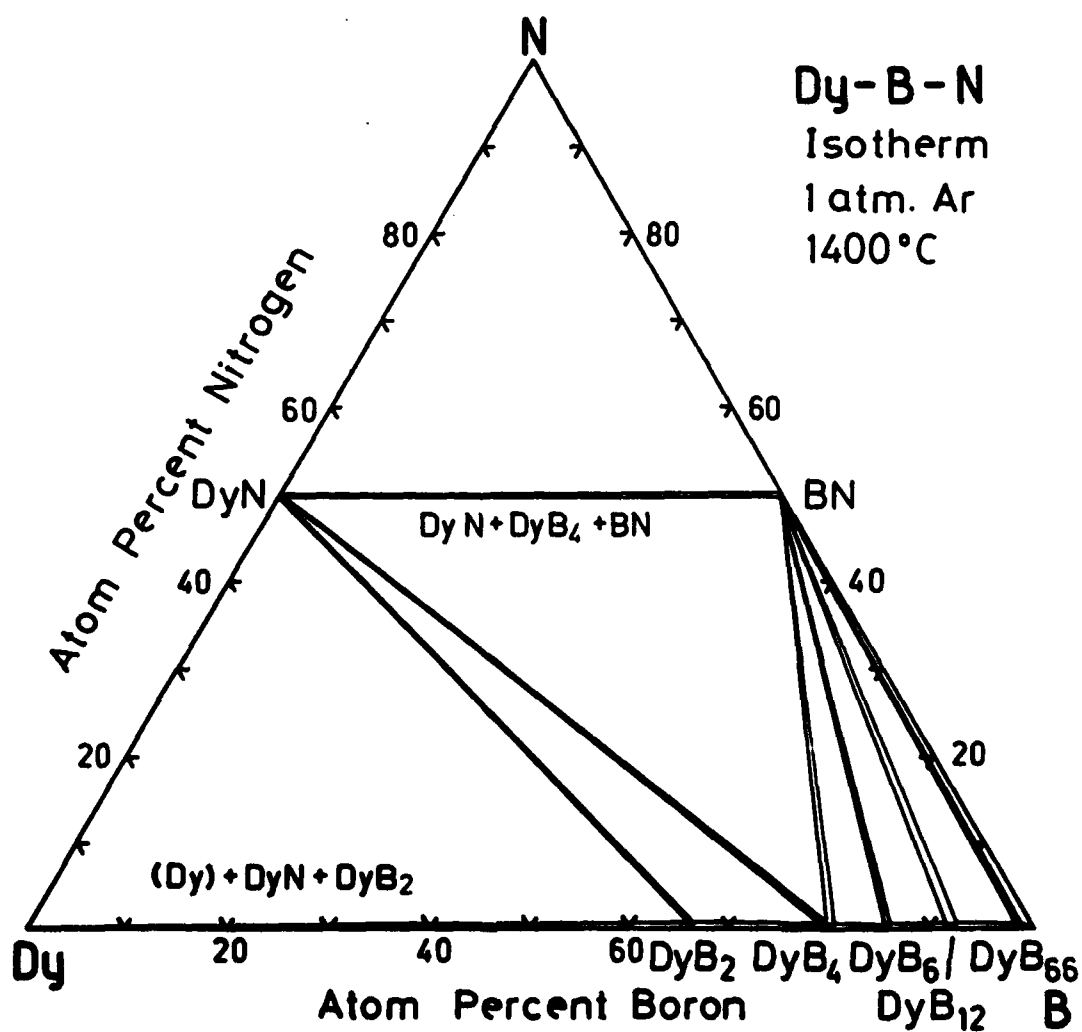
## REFERENCES

- [72Kie] R.Kieffer, P. Ettmayer and S. Pajakoff, "On The Mononitrides and on Nitrogen-rich Nitrides of the Rare Earths, 1<sup>st</sup> Commun.", (in German), Monatsh. Chemie 103 (1972) 1285-1298
- [76Spe] K. E. Spear, "Phase Behavior and Related Properties of Rare Earth Borides", in "Phase Diagrams in Materials Science and Technology", Ed. A.M.Alper, (Acad. Press, NY, 1976) 91-159
- [78Fro] E. Fromm, H. Jehn and G. Hoerz, "Gases and Carbon in Metals" ZAED, Physics Data, 5-3 (1978) pp 2
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, Oh, 1985)
- [89Rem] K. Remschnig and P.Rogl, "The Ternary Systems: Rare Earth - Aluminium - Boron, RE=Y,La,Ce,Pr,Nd,Gd,Tb,Dy,Ho,Er and Tm", Proceedings of the 12<sup>th</sup> Plansee Seminar, Eds. H.Bildstein and H. Ortner, ( Tyrolia Verlag, Innsbruck, Austria ), Vol II, (1989) 599-607
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met.Intl., Metals Park, Oh, 1990)
- [91Kle] H. Klesnar and P.Rogl, "Phase Relations in The Ternary Systems Rare Earth (RE)-Boron-Nitrogen, RE=Tb through Lu and Sc,Y", High Temperatures-High Pressures, (1991) in press

Table 1: Solid phases at 1400°C in the system B-Dy-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\beta$ -Dy 1409-1381°	cI2 Im $\bar{3}$ m W	a= 398	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vi1] [85Vi1]
DyB <sub>2</sub> <2100°	hP3 P6/mmm AlB <sub>2</sub>	a= 328.7 c= 384.5	[85Vi1]
DyB <sub>4</sub> <2500°	tP20 P4/mbm ThB <sub>4</sub>	a= 702.1 c= 397.2	[85Vi1]
DyB <sub>6</sub> <2200°	cP7 Fm $\bar{3}$ m CaB <sub>6</sub>	a= 409.8	[85Vi1]
DyB <sub>12</sub> <2100°	cF52 Fm $\bar{3}$ m UB <sub>12</sub>	a= 749.9	[85Vi1]
DyB <sub>66</sub> <2025°	cF1608 Fm $\bar{3}$ c YB <sub>66</sub>	a=2344.1	[85Vi1]
DyN	cF8 Fm $\bar{3}$ m NaCl	a= 493.6	[85Vi1]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vi1]

Fig.1: Isothermal section of the system B - Dy -N at 1400°C under 1 bar of argon ( in the absence of external nitrogen ).



## SYSTEM BORON- HOLMIUM- NITROGEN (B-Ho-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Ho-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than  $20\mu\text{m}$  in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace ( under 1 bar of 5N-Ar or 5N-N<sub>2</sub> ) usually consisted of a primary reaction at  $1200^{\circ}\text{C}$  for 90h followed by a final reaction at  $1400^{\circ}\text{C}$  for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. ue to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O<sub>2</sub> and  $< 4$  ppm H<sub>2</sub>O. Starting materials were ingots of 3N-Y, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at  $1400^{\circ}\text{C}$ . Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [91Kle].

### BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Ho system revealed consistency with the data available in [76Spe], [84Vil] and [90Mas]; see Table 1. Mutual solid solubilities are expected to be negligible. HoB<sub>6</sub> has been found to be unstable below  $1450^{\circ}\text{C}$  [89Rem].

No equilibrium diagram exists for the N-Ho system and solid solubility of N in Ho is said to be small; a comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure HoN is the only stable nitride (see Table 1), at higher nitrogen pressure HoN<sub>2-3</sub> with the Mn<sub>2</sub>O<sub>3</sub>-type (c180 - 1a3, a=1056 pm ) has been reported [72Kie].

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at  $1400^{\circ}\text{C}$  under 1 bar of argon (in the absence of external nitrogen pressure) [91Kle]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium  $\text{HoN} + \text{HoB}_4 + \text{BN}$ . Thus there is no compatibility between (Ho) and BN. As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Ho in BN at  $1400^{\circ}\text{C}$ , and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91Kle].

No signs of compound formation at higher nitrogen contents were observed [91Kle] from heat treatments under 1 bar of  $\text{N}_2$  at  $1400^{\circ}\text{C}$  (100h) and at  $1800^{\circ}\text{C}$  (20h) respectively : in both cases the limiting tie line reported was  $\text{HoN} + \text{BN}$ .



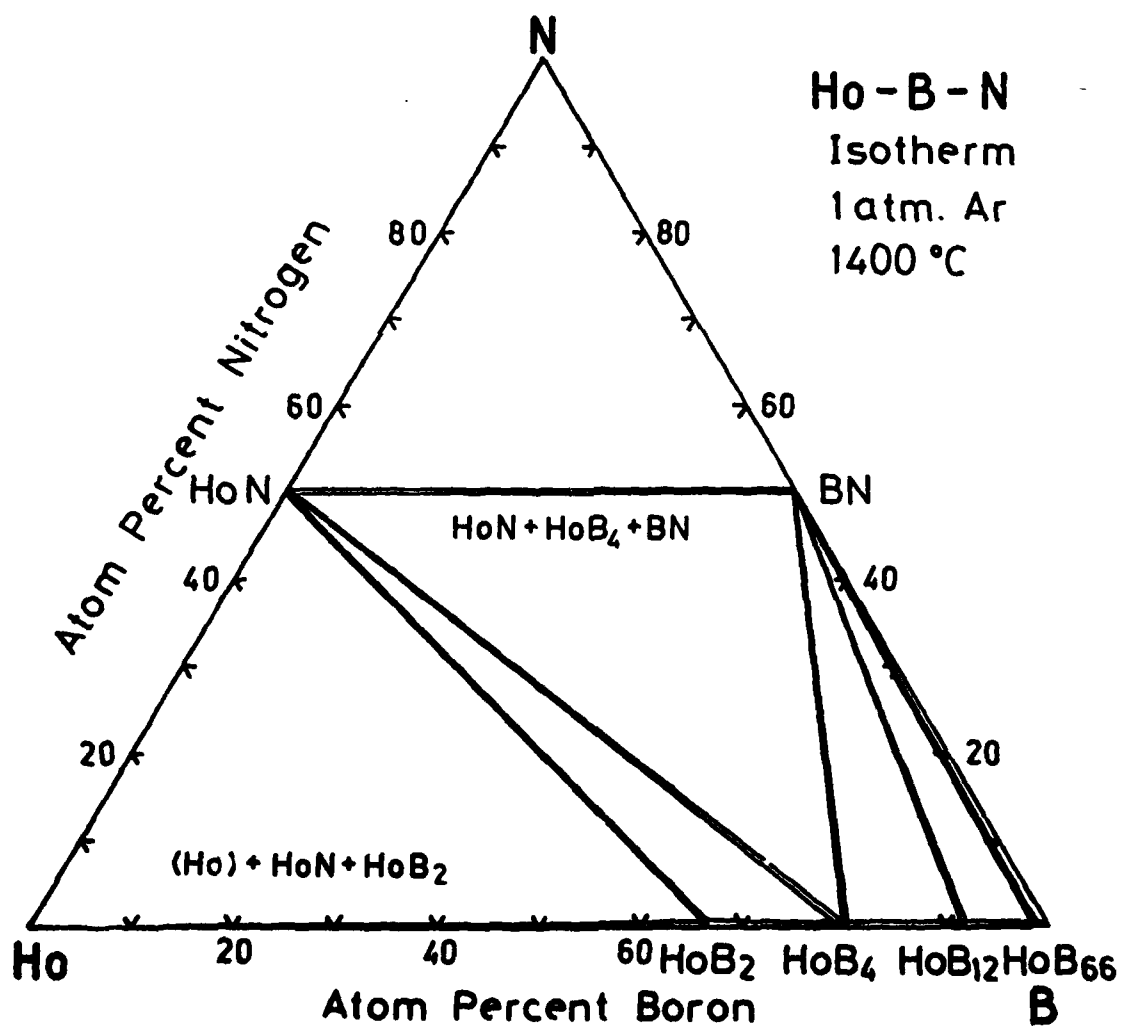
## REFERENCES

- [72Kie] R.Kieffer, P. Ettmayer and S. Pajakoff, "On The Mononitrides and on Nitrogen-rich Nitrides of the Rare Earths, 1<sup>st</sup> Commun.", (in German), Monatsh. Chemie 103 (1972) 1285-1298
- [76Spe] K. E. Spear, "Phase Behavior and Related Properties of Rare Earth Borides", in "Phase Diagrams in Materials Science and Technology", Ed. A.M.Alper, (Acad. Press, NY, 1976) 91-159
- [78Fro] E. Fromm, H. Jehn and G. Hoerz, "Gases and Carbon in Metals" ZAED, Physics Data, 5-3 (1978) pp 2
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, Oh, 1985)
- [89Rem] K. Remschnig and P.Rogl, "The Ternary Systems: Rare Earth - Aluminium - Boron, RE=Y,La,Ce,Pr,Nd,Gd,Tb,Dy,Ho,Er and Tm", Proceedings of the 12<sup>th</sup> Plansee Seminar, Eds. H.Bildstein and H. Ortner, ( Tyrolia Verlag, Innsbruck, Austria ), Vol II, (1989) 599-607
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met.Intl., Metals Park, Oh, 1990)
- [91Kle] H. Klesnar and P.Rogl, "Phase Relations in The Ternary Systems Rare Earth (RE) - Boron - Nitrogen, RE=Tb through Lu and Sc,Y", High Temperatures-High Pressures, (1991) in press

Table 1: Solid phases at 1400°C in the system B-Ho-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Ho <1470°	hP2 P6 <sub>3</sub> /mmc Mg	a= 357.78 c= 561.78	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}m$ $\beta$ -B	a=1092.51 c=2381.43	[85Vi1]
HoB <sub>2</sub> <2200°	hP3 P6/mmm AlB <sub>2</sub>	a= 327.3 c= 381.4	[85Vi1]
HoB <sub>4</sub> <2500°	tP20 P4/mbm ThB <sub>4</sub>	a= 708.7 c= 400.8	[85Vi1]
HoB <sub>12</sub> 2100°	cF52 Fm $\bar{3}m$ UB <sub>12</sub>	a= 749.1	[85Vi1]
HoB <sub>∞</sub> <2025°	cF1608 Fm $\bar{3}c$ YB <sub>∞</sub>	a=2344.1	[85Vi1]
HoN	cF8 Fm $\bar{3}m$ NaCl	a= 487.7	[85Vi1]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vi1]

Fig.1: Isothermal section of the system B - Ho - N at 1400°C under 1 bar of argon ( in the absense of external nitrogen ).



## SYSTEM BORON- ERBIUM- NITROGEN (B-Er-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Er-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than  $20\mu\text{m}$  in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace ( under 1 bar of 5N-Ar or 5N-N<sub>2</sub> ) usually consisted of a primary reaction at  $1200^{\circ}\text{C}$  for 90h followed by a final reaction at  $1400^{\circ}\text{C}$  for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O<sub>2</sub> and  $< 4$  ppm H<sub>2</sub>O. Starting materials were ingots of 3N-Er, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at  $1400^{\circ}\text{C}$ . Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [91Kle].

### BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Er system revealed consistency with the data available in [76Spe], [84Vil] and [90Mas]; see Table 1. Mutual solid solubilities are expected to be negligible.

No equilibrium diagram exists for the N-Er system and solid solubility of N in Er is said to be small; a comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure ErN is the only stable nitride (see Table 1), at higher nitrogen pressure Er<sub>2</sub>N<sub>3-x</sub> with the Mn<sub>2</sub>O<sub>3</sub>-type (c180 - 1a3) has been reported [72Kle].

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at  $1400^{\circ}\text{C}$  under 1 bar of argon (in the absence of external nitrogen pressure) [91Kle]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium  $\text{ErN} + \text{ErB}_4 + \text{BN}$ . Thus there is no compatibility between (Er) and BN. As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Er in BN at  $1400^{\circ}\text{C}$ , and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91Kle].

No signs of compound formation at higher nitrogen contents were observed [91Kle] from heat treatments under 1 bar of  $\text{N}_2$  at  $1400^{\circ}\text{C}$  (100h) and at  $1800^{\circ}\text{C}$  (20h) respectively :in both cases the limiting tie line reported was  $\text{ErN} + \text{BN}$ .

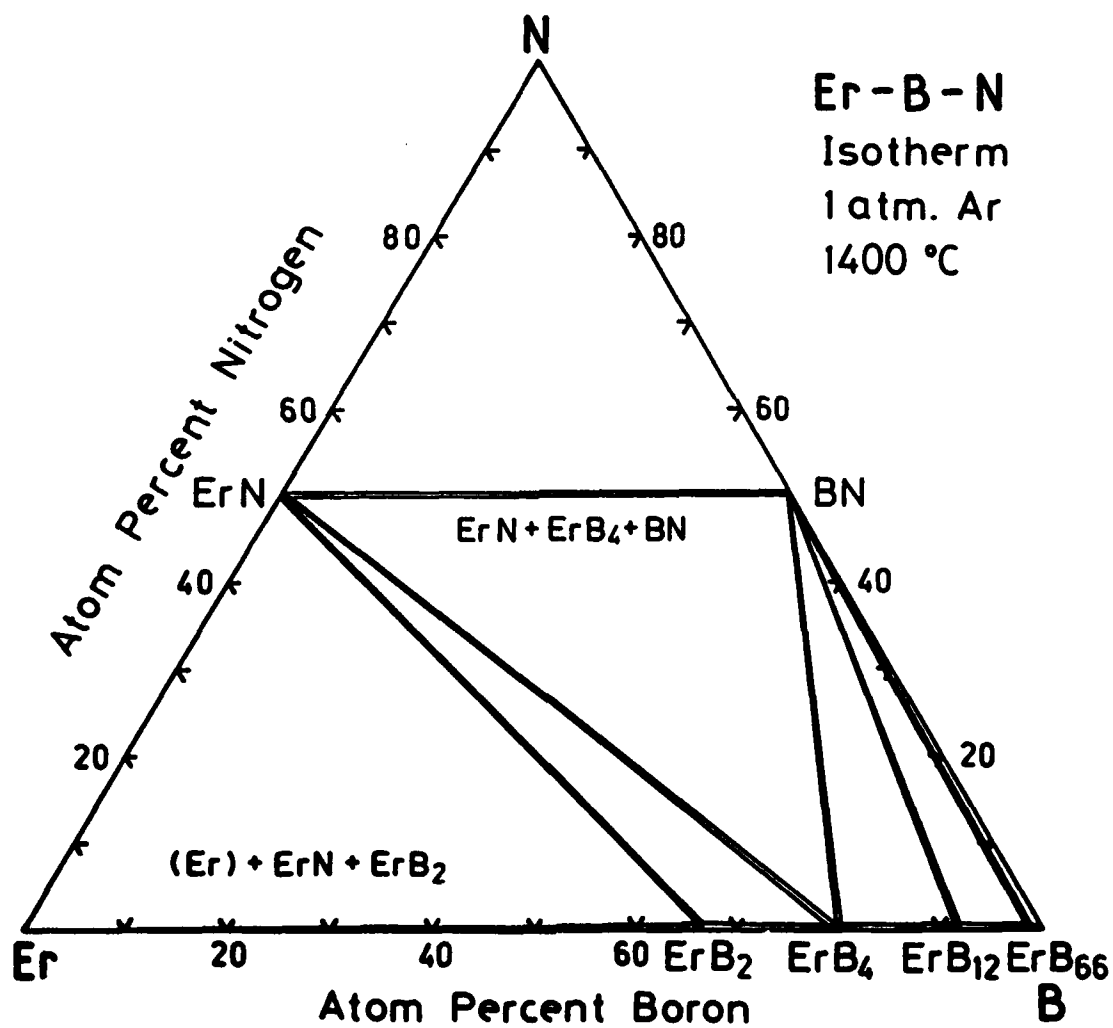
## REFERENCES

- [72Kie] R.Kieffer, P. Ettmayer and S. Pajakoff, "On The Mononitrides and on Nitrogen-rich Nitrides of the Rare Earths, 1<sup>st</sup> Commun.", (in German), Monatsh. Chemie 103 (1972) 1285-1298
- [76Spe] K. E. Spear, "Phase Behavior and Related Properties of Rare Earth Borides", in "Phase Diagrams in Materials Science and Technology", Ed. A.M.Alper, (Acad. Press, NY, 1976) 91-159
- [78Fro] E. Fromm, H. Jehn and G. Hoerz, "Gases and Carbon in Metals" ZAED, Physics Data,5-3 (1978) pp 2
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met.,Metals Park, Oh, 1985)
- [89Rem] K. Remschnig and P.Rogl, "The Ternary Systems: Rare Earth - Aluminium - Boron, RE=Y,La,Ce,Pr,Nd,Gd,Tb,Dy,Ho,Er and Tm", Proceedings of the 12<sup>th</sup> Plansee Seminar, Eds. H.Bildstein and H. Ortner, ( Tyrolia Verlag, Innsbruck,Austria ), Vol II, (1989) 599-607
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met.Intl., Metals Park,Oh, 1990)
- [91Kle] H. Klesnar and P.Rogl, "Phase Relations in The Ternary Systems Rare Earth (RE)-Boron-Nitrogen, RE=Tb through Lu and Sc,Y", High Temperatures-High Pressures, (1991) in press

Table 1: Solid phases at 1400°C in the system B-Er-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Er <1522°	hP2 P6 <sub>3</sub> /mmc Mg	a= 355.92 c= 558.50	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}m$ $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
ErB <sub>2</sub> <2185°	hP3 P6/mmm AlB <sub>2</sub>	a= 326.5 c= 376.8	[85Vil]
ErB <sub>4</sub> <2500°	tP20 P4/nbm ThB <sub>4</sub>	a= 707.05 c= 400.00	[85Vil]
ErB <sub>12</sub> <2080°	cF52 Fm $\bar{3}m$ UB <sub>12</sub>	a= 748.2	[85Vil]
ErB <sub>66</sub> <2070°	cF1608 Fm $\bar{3}c$ YB <sub>66</sub>	a=2344.0	[85Vil]
ErN	cF8 Fm $\bar{3}m$ NaCl	a= 483.6	[85Vil]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section of the system B - Er -N at 1400°C under 1 bar of argon ( in the absence of external nitrogen ).





## INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Tm-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than  $20\mu\text{m}$  in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N<sub>2</sub>) usually consisted of a primary reaction at  $1200^{\circ}\text{C}$  for 90h followed by a final reaction at  $1400^{\circ}\text{C}$  for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O<sub>2</sub> and  $< 4$  ppm H<sub>2</sub>O. Starting materials were ingots of 3N-Tm, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at  $1400^{\circ}\text{C}$ . Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [91Kle].

## BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Tm system revealed consistency with the data available in [76Spe], [84Vil] and [90Mas]; see Table 1. Mutual solid solubilities are expected to be negligible.

No equilibrium diagram exists for the N-Tm system and solid solubility of N in Tm is said to be small; a comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure TmN is the only stable nitride (see Table 1); at higher nitrogen pressure  $\text{Tm}_2\text{N}_{3-x}$  with the  $\text{Mn}_2\text{O}_3$ -type (c180 -  $1a\bar{3}$ ,  $a=1045$  pm) has been reported [72Kle].

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at  $1400^{\circ}\text{C}$  under 1 bar of argon (in the absence of external nitrogen pressure) [91Kle]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium  $\text{TmN} + \text{TmB}_4 + \text{BN}$ . Thus there is no compatibility between (Tm) and BN. As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Tm in BN at  $1400^{\circ}\text{C}$ , and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91Kle].

No signs of compound formation at higher nitrogen contents were observed [91Kle] from heat treatments under 1 bar of  $\text{N}_2$  at  $1400^{\circ}\text{C}$  (100h) and at  $1800^{\circ}\text{C}$  (20h) respectively :in both cases the limiting tie line reported was  $\text{TmN} + \text{BN}$  .

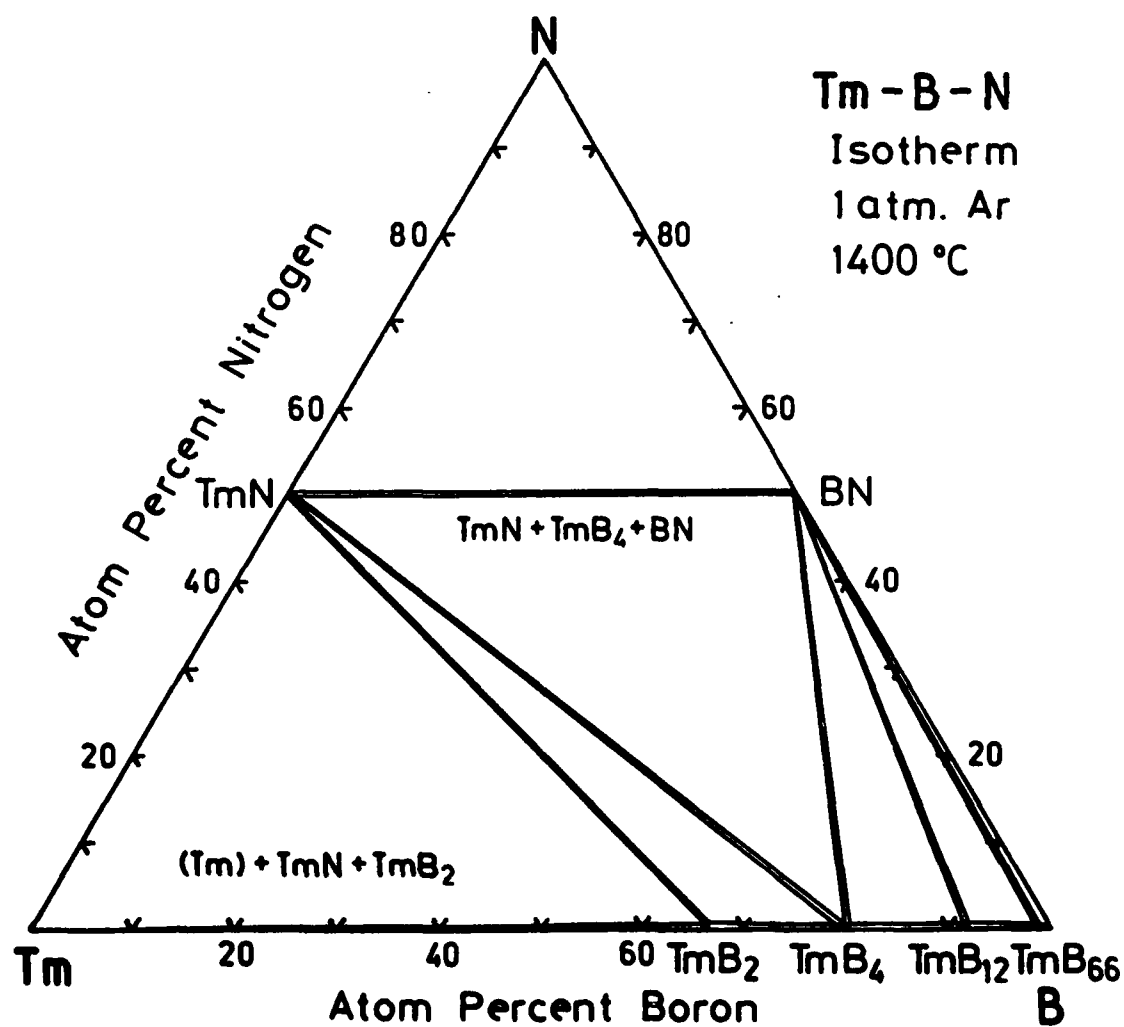
## REFERENCES

- [72Kie] R.Kieffer, P. Ettmayer and S. Pajakoff, "On The Mononitrides and on Nitrogen-rich Nitrides of the Rare Earths, 1<sup>st</sup> Commun.", (in German), Monatsh. Chemie 103 (1972) 1285-1298
- [76Spe] K. E. Spear, "Phase Behavior and Related Properties of Rare Earth Borides", in "Phase Diagrams in Materials Science and Technology", Ed. A.M.Alper, (Acad. Press, NY, 1976) 91-159
- [78Fro] E. Fromm, H. Jehn and G. Hoerz, "Gases and Carbon in Metals" ZAED, Physics Data,5-3 (1978) pp 2
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met.,Metals Park, Oh, 1985)
- [89Rem] K. Remschnig and P.Rogl, "The Ternary Systems: Rare Earth - Aluminium - Boron, RE=Y,La,Ce,Pr,Nd,Gd,Tb,Dy,Ho,Er and Tm", Proceedings of the 12<sup>th</sup> Plansee Seminar, Eds. H.Bildstein and H. Ortner, ( Tyrolia Verlag, Innsbruck,Austria ), Vol II, (1989) 599-607
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met.Intl., Metals Park,Oh, 1990)
- [91Kle] H. Klesnar and P.Rogl, "Phase Relations in The Ternary Systems Rare Earth (RE) - Boron - Nitrogen, RE=Tb through Lu and Sc,Y", High Temperatures-High Pressures, (1991) in press

Table 1: Solid phases at 1400°C in the system B-Tm-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Tm <1545°	hP2 P6 <sub>3</sub> /mmc Mg	a= 353.75 c= 555.40	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}m$ $\beta$ -B	a=1092.51 c=2381.43	[85Vi1] [85Vi1]
TmB <sub>2</sub> 2250°	hP3 P6/mmm AlB <sub>2</sub>	a= 326.1 c= 375.5	[85Vi1]
TmB <sub>4</sub> <2550°	tP20 P4/mbm ThB <sub>4</sub>	a= 705.7 c= 398.7	[85Vi1]
TmB <sub>12</sub> <2180°	cF52 Fm $\bar{3}m$ UB <sub>12</sub>	a= 747.4	[85Vi1]
TmB <sub>66</sub> <2100°	cF1608 Fm $\bar{3}c$ YB <sub>66</sub>	a=2343.3	[85Vi1]
TmN	cFB Fm $\bar{3}m$ NaCl	a= 481	[85Vi1]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vi1]

Fig.1: Isothermal section of the system B - Tm -N at 1400°C under 1 bar of argon ( in the absence of external nitrogen ).



## INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Lu-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than  $20\mu\text{m}$  in a steel mortar and/or a WC-Co mortar respectively [91Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace ( under 1 bar of 5N-Ar or 5N-N<sub>2</sub> ) usually consisted of a primary reaction at  $1200^{\circ}\text{C}$  for 90h followed by a final reaction at  $1400^{\circ}\text{C}$  for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O<sub>2</sub> and < 4 ppm H<sub>2</sub>O. Starting materials were ingots of 3N-Lu, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at  $1400^{\circ}\text{C}$ . Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [91Kle].

## BINARY SYSTEMS

A recent reinvestigation [89Rem] of the B-Lu system revealed consistency with the data available in [76Spe], [84Vil] and [90Mas]; see Table 1. Mutual solid solubilities are expected to be negligible.

No equilibrium diagram exists for the N-Lu system and solid solubility of N in Lu is said to be small; a comprehensive discussion of all reported information has been given by [78Fro]. At normal pressure LuN is the only stable nitride (see Table 1), at higher nitrogen pressure Lu<sub>2</sub>N<sub>3-x</sub> with the Mn<sub>2</sub>O<sub>3</sub>-type (c180 - Ia $\bar{3}$ , a=1032 pm ) has been reported [72Kie].

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at  $1400^{\circ}\text{C}$  under 1 bar of argon (in the absence of external nitrogen pressure) [91Kle]. Phase equilibria are characterized by the absence of ternary compounds and by the formation of a three-phase equilibrium  $\text{LuN} + \text{LuB}_2 + \text{BN}$ . Thus there is no compatibility between (Lu) and BN. As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Lu in BN at  $1400^{\circ}\text{C}$ , and mutual solubilities of the rare earth borides, the rare earth nitride and BN are rather restricted [91Kle].

No signs of compound formation at higher nitrogen contents were observed [91Kle] from heat treatments under 1 bar of  $\text{N}_2$  at  $1400^{\circ}\text{C}$  (100h) and at  $1800^{\circ}\text{C}$  (20h) respectively :in both cases the limiting tie line reported was  $\text{LuN} + \text{BN}$ .

## REFERENCES

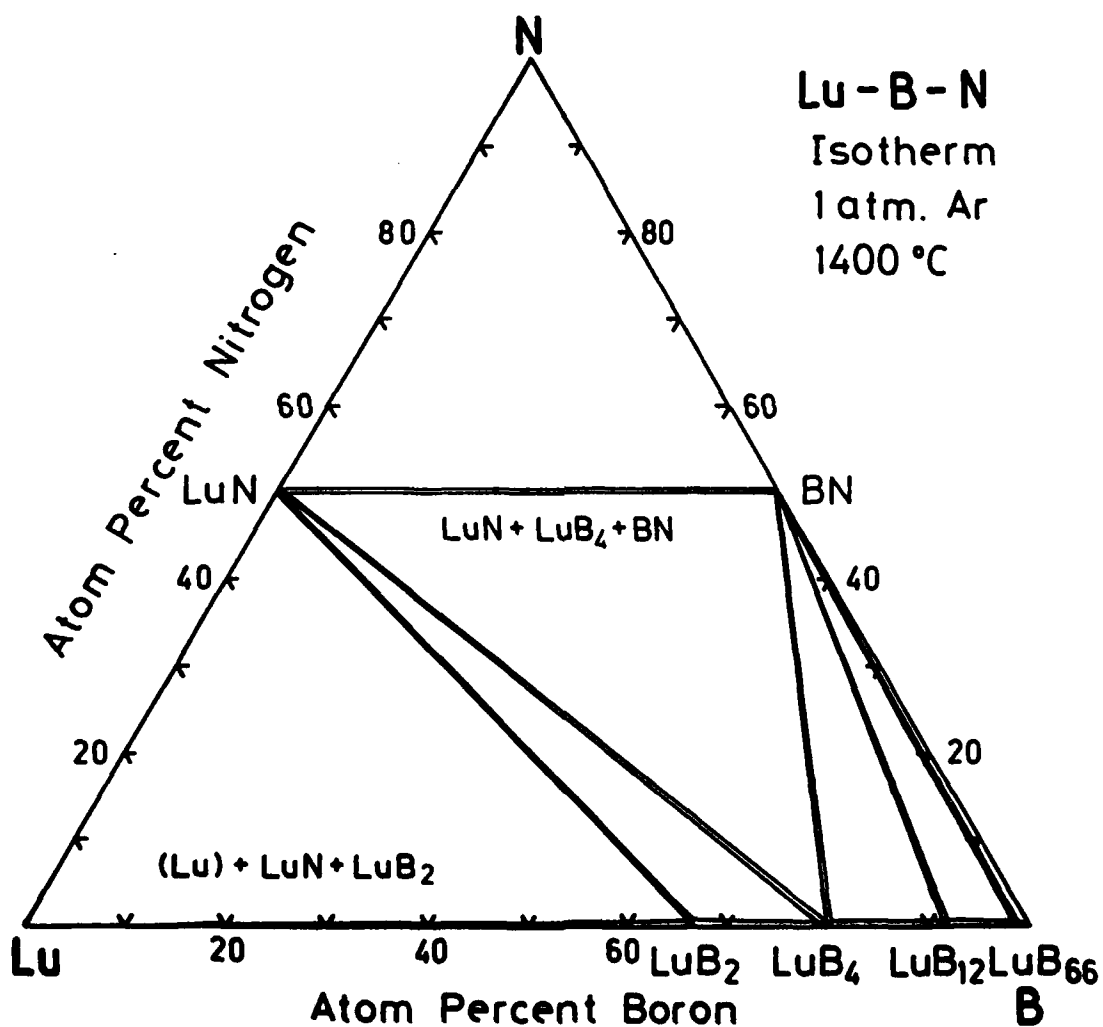
- [72Kie] R.Kieffer, P. Ettmayer and S. Pajakoff, "On The Mononitrides and on Nitrogen-rich Nitrides of the Rare Earths, 1<sup>st</sup> Commun.", (in German), Monatsh. Chemie 103 (1972) 1285-1298
- [76Spe] K. E. Spear, "Phase Behavior and Related Properties of Rare Earth Borides", in "Phase Diagrams in Materials Science and Technology", Ed. A.M.Alper, (Acad. Press, NY, 1976) 91-159
- [78Fro] E. Fromm, H. Jehn and G. Hoerz, "Gases and Carbon in Metals" ZAED, Physics Data, 5-3 (1978) pp 2
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, Oh, 1985)
- [89Rem] K. Remschnig and P.Rogl, "The Ternary Systems: Rare Earth - Aluminium - Boron, RE=Y,La,Ce,Pr,Nd,Gd,Tb,Dy,Ho,Er and Tm", Proceedings of the 12<sup>th</sup> Plansee Seminar, Eds. H.Bildstein and H. Ortner, ( Tyrolia Verlag, Innsbruck,Austria ), Vol. II, (1989) 599-607
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met.Intl., Metals Park,Oh, 1990)
- [91Kle] H. Klesnar and P.Rogl, "Phase Relations in The Ternary Systems Rare Earth (RE) - Boron - Nitrogen, RE=Tb through Lu and Sc,Y", High Temperatures-High Pressures, (1991) in press



Table 1: Solid phases at 1400°C in the systems B - Lu - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Lu <1663°	hP2 P6 <sub>3</sub> /mmc Mg	a= 350.52 c= 554.94	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
LuB <sub>2</sub> <2250°	hP3 P6/mmm AlB <sub>2</sub>	a= 324.6 c= 370.4	[85Vil]
LuB <sub>4</sub> <2550°	tP20 F4/mbm ThB <sub>4</sub>	a= 703.6 c= 397.4	[85Vil]
LuB <sub>12</sub> <2170°	cF52 Fm $\bar{3}$ m UB <sub>12</sub>	a= 746.4	[85Vil]
LuB <sub>66</sub> <2100°	cF1608 Fm $\bar{3}$ c YB <sub>66</sub>	a=2341.2	[85Vil]
LuN	cF8 Fm $\bar{3}$ m NaCl	a= 476.6	[85Vil]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section of the system B - Lu -N at 1400°C under 1 bar of argon ( in the absence of external nitrogen ).



## SYSTEM BORON - URANIUM - NITROGEN (B-U-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-U-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20 $\mu$ m in a steel mortar and/or a WC-Co mortar respectively [90Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace ( under 1 bar of 5N-Ar or 5N-N<sub>2</sub> ) usually consisted of a primary reaction at 1200°C for 90h followed by a final reaction at 1400°C for 90h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Due to the pronounced instability of the binary metal nitride with respect to rapid hydrolysis in moist environment, all handling of the specimens was done in an argon filled glove box system ensuring an oxygen level of less than 2 ppm O<sub>2</sub> and < 4 ppm H<sub>2</sub>O. Starting materials were platelets of depleted uranium (E.Merck, FRG) which prior to use were surface cleaned in dilute HNO<sub>3</sub>, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [90Kle].

### BINARY SYSTEMS

A reinvestigation of the binary systems revealed consistency with the data available in [85Vil], and [90Mas] (see Table 1); for a recent critical assessment of the U - B binary see [91Pot].

The phase diagram N-U is given by [90Mas], see also Table 1; the maximal solid solubility of N in  $\alpha$ ,  $\beta$  or  $\gamma$ -U was claimed to be less than 0.017at% N [78Fro].

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at  $1400^{\circ}\text{C}$  under 1 bar of argon (in the absence of external nitrogen pressure) [90K1e]. Phase equilibria are characterized by the existence of one of ternary compound UBN (isotypic with the structure type of UBC). Due to the formation of the stable three-phase equilibria:  $\text{UB}_2 + \text{UBN} + \text{UN}$  and  $\text{UB}_4 + \text{UBN} + \text{BN}$ , no compatibility was observed between (U) and BN nor between the uranium nitrides and boron. From the close correspondance of the unit cell dimensions of the boundary phases in multiphase samples with the data for the binary compounds no significant solid solubility of N ( $< 0.5\text{at\% N}$ ) in the uranium borides was concluded. Similarly solid solubility of U in BN at  $1400^{\circ}\text{C}$  was considered to be rather limited. No significant trends have been observed for the variation of the unit cell dimensions of the binary uranium nitrides as a function of the boron content [90K1e], thus the solid solubility of B is certainly smaller than originally suggested by [76Imo].

From heat treatments under 1 bar of  $\text{N}_2$  at  $1400^{\circ}\text{C}$  (90h) the limiting tie line reported was between uranium nitride and boronnitride. Mutual solid solubilities remained restricted. Additional heat treatment for 60h at  $1400^{\circ}\text{C}$  in a high vacuum of  $10^{-4}\text{Pa}$  was sufficient to entirely decompose the ternary compound UBN, and all nitrogen-rich samples were transferred to the tie lines  $\text{UN} + \text{UB}_2$  and  $\text{UB}_4 + \text{BN}$ . X-ray Guinier photographs of UBN were completely indexed on the basis of an orthorhombic unit cell in close correspondance with the UBC-type. Using the atom parameters derived from a single crystal study of stoichiometric UBC [91Rog], calculated and observed intensity data were said to be in excellent agreement for UBN [90K1e]. The variation of the unit cell dimensions of UBN, as observed from multiphase samples at  $1400^{\circ}\text{C}$  as well as under various  $\text{N}_2$  partial pressures is rather small indicating only a small degree of boron/nitrogen substitution [90K1e].

## REFERENCES

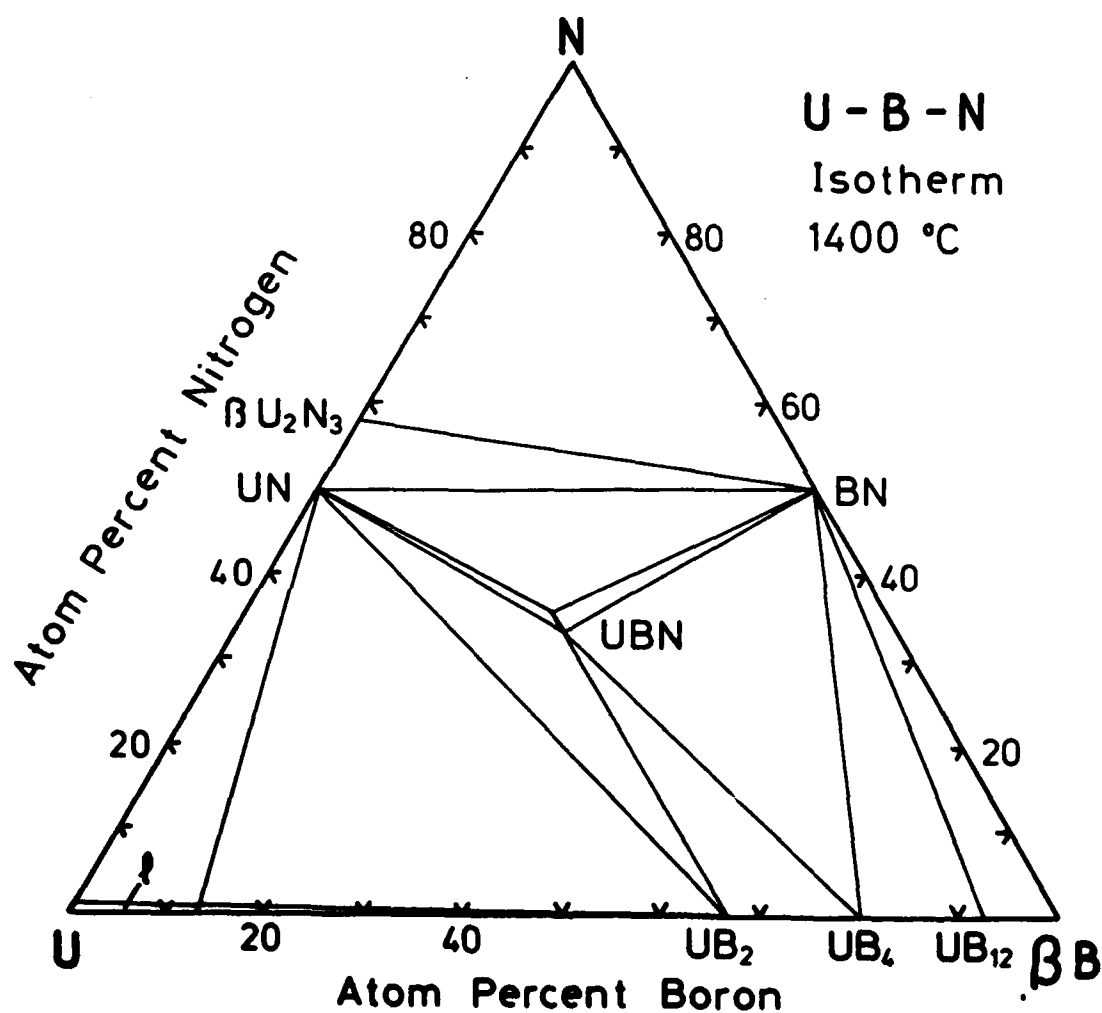
- [67Imo] T. Imoto, K. Niihara, and H.J.Stoecker, "Solid Solubility in NaCl-type Uranium Compounds", in "Thermodynamics of Nuclear Materials", Proceedings of Symposium, Vienna, Sept. 1967, published by IAEA-1968, 371-383
- [78Fro] E. Fromm, H. Jehn and G. Hoerz, "Gases and Carbon in Metals" ZAED, Physics Data,5-3 (1978) pp 2
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met.,Metals Park, Oh,1985)
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met.Intl., Metals Park,Oh, 1990)
- [90Kle] H. Klesnar and P.Rogl, "The Ternary System Uranium - Boron - Nitrogen", Proceedings of the 12<sup>th</sup> Intl. Symposium on Boron, Borides and Related Compounds, Albuquerque, USA, August 1990.
- [91Pot] P.E.Potter, "Binary Actinoid Borides" in "the Handbook on the Physics and Chemistry of the Actinides" (A.Freeman and C.Keller,Eds; North Holland, Amsterdam,N.Y.),Vol. 7, (1991)

Table 1: Solid phases at 1400°C in the system B-U-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\gamma$ -U 1135-776°	cI2 Im $\bar{3}$ m W	a= 352.4	[90Mas]
$\beta$ -U 776-668°	tP30 P4 <sub>2</sub> /mm $\beta$ -U	a=1075.9 c= 565.6	[90Mas]
$\alpha$ -U <668°	oC4 Cmcm $\alpha$ -U	a= 285.37 b= 586.95 c= 495.48	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
UB <sub>2</sub> <2385°	hP3 P6/mmm AlB <sub>2</sub>	a= 312.93 c= 398.53	[91Pot], U-rich
UB <sub>4</sub> <2495°	tP20 P4/mbm ThB <sub>4</sub>	a= 313.14 c= 398.57 a= 707.7 c= 397.9	[91Pot], U-poor [91Pot]
UB <sub>12</sub> <2235°	cF52 Fm $\bar{3}$ m UB <sub>12</sub>	a= 747.0 a= 747.4	[91Pot], U-rich [91Pot], U-poor
UN <2805°	cF8 Fm $\bar{3}$ m NaCl	a= 488.94	[91Pot]
$\beta$ -U <sub>2</sub> N <sub>8</sub> 1352-1000°	cI80 Ia $\bar{3}$ Mn <sub>2</sub> O <sub>8</sub>	a=1068	[85Vil]

$\alpha\text{-U}_2\text{N}_3$ <1132°	hP5 $P\bar{3}m1$ $\text{La}_2\text{O}_3$	a= 370 c= 582.5	[85Vil]
BN <sub>hex</sub>	- BN	a=250.4 c=666.1	[85Vil]
* UBN	oC12 Cmcm UBC	a=358.51 b=1182.73 c=332.54	[90Kle]

Fig.1: Isothermal section of the system B - U - N at 1400°C under 1 bar of argon ( in the absense of external nitrogen ).





## SYSTEM BORON - TITANIUM - NITROGEN (B-Ti-N)

### INTRODUCTION / EXPERIMENTAL

Informations on the Ti-B-N ternary are due to [55Bre,61Now], [73Sam,80Yur,81Chu,83Tka,84Bor] and [87Smi] with an early review by [72Med].

Based on an early thermodynamic estimation of the reaction  $\text{TiN} + 2 \text{BN} \rightleftharpoons \text{TiB}_2 + \frac{3}{2} \text{N}_2$  under  $0.5 \cdot 10^5 \text{ Pa}$  of nitrogen, [55Bre] proposed stability of the mixture  $\text{TiN} + \text{BN}$  up to ca  $1600^\circ\text{C}$ . Accordingly phase equilibria at  $1500^\circ\text{C}$  under argon of 0.1%  $\text{N}_2$  as derived by [61Now] are characterized by the absence of ternary boronitride compounds and by a dominating three phase field  $\text{TiB}_2 + \text{TiN}_{1-x} + \text{BN}$ . Based on these data [80Yur] determined the heat of formation of  $\text{TiB}_2$  via the experimentally monitored decomposition reaction of powder compacts  $\text{TiN} + 2 \text{BN}$  in the temperature range  $1575$  to  $1850^\circ\text{C}$  as a function of temperature. For equilibrium pressures of  $100 \text{ Pa N}_2$  the decomposition was found to commence at ca  $1350^\circ\text{C}$  [80Yur]. These data are in essential agreement with a DTA study revealing the onset of decomposition at ca  $1375$  to  $1440^\circ\text{C}$  [84Bor].

[81Chu] claimed the existence of a quasibinary section of the eutectic type  $\text{TiB}_2 + \text{TiN}$  revealing small mutual solid solubilities at the nitrogen-rich phase boundary  $\text{TiN}_{0.99}$ , whereas solubility of  $\text{TiB}_2$  in  $\text{TiN}_{0.99}$  was said to increase up to ca 12 mol% at  $2300^\circ\text{C}$ .

Phase equilibria in the B-Ti-N system have been furthermore investigated [87Smi] at  $1500^\circ$  under high vacuum or 1 bar Ar or under 1 bar  $\text{N}_2$  respectively. Phase relations have been established from room temperature X-ray powder diffraction analysis of about 10 binary and 25 ternary samples prepared by reaction sintering of cold compacted powder blends of B, BN, Ti, TiN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than  $20 \mu\text{m}$  in a steel mortar and/or a WC-Co mortar respectively [87Smi]. For annealing in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N- $\text{N}_2$ ) the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments usually consisted of a primary reaction at  $1500^\circ\text{C}$  for 72h followed by a final reaction at  $1500^\circ\text{C}$  up to 144h with an intermediate step of crushing and

recompacting to ensure homogeneity. After heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Ti, crystallized boron (99.8 % B),  $\text{TiN}_{1-x}$  (99.8%) and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at  $1400^{\circ}\text{C}$ . Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [87Šmi].

## BINARY SYSTEMS

The reinvestigation [87Šmi] of the B-Ti system in the range from 900 to  $2400^{\circ}\text{C}$  revealed consistency with the data available in [84Vil], and [90Mas]; a critical assessment is due to [86Mur]. The existence of  $\text{Ti}_3\text{B}_4$  has been confirmed [87Šmi]. The maximal solid solubility of boron in titanium was claimed to be less than 1 at%B at  $1540^{\circ}\text{C}$  [66Rud] and an interstitial type of B-solubility was suggested. The maximum solid solubility of Ti in  $\beta$ -B was reported to be less than 0.5 at% Ti at  $\sim 1800^{\circ}\text{C}$  from X-ray powder data [70Car] (see Table 1).

The phase diagram for the system Ti-N as given in [90Mas] has to be modified according to [90Len] regarding the newly discovered phases  $\text{Ti}_3\text{N}_{2-x}$  and  $\text{Ti}_4\text{N}_{3-x}$  [86Len1,2].

Crystallographic information on the binary titanium compounds is found in Table 1.

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 summarizes the results on the phase relations Ti-B-N at  $1500^{\circ}\text{C}$  under 1 bar Ar as observed by [61Now] and confirmed by [87Šmi]. Phase equilibria are characterized by the absence of ternary compounds and by incompatibility of titanium metal and  $\text{BN}_{\text{hex}}$  due to the formation of a stable tie line  $\text{TiB} - \text{TiN}_{1-x}$  at temperatures below  $1500^{\circ}\text{C}$ . Heating binary as well as ternary alloys at  $1500^{\circ}\text{C}$  under 1 bar  $\text{N}_2$  transfers all samples to the limiting tie line at the nitrogen rich boundary  $\text{TiN} + \text{BN}$ , equilibrium being reached after 75h of nitrogen exposure [87Šmi].

As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Ti in BN up to  $1500^{\circ}\text{C}$ , and mutual

solubilities of the titanium borides, the titanium nitrides and BN up to 1500°C are rather restricted [87Sm].

## THERMODYNAMICS

A thermodynamic modelling of the binary system Ti-B is due to [86Mur]; see Table 2. The enthalpy of formation of  $TiB_2$  as derived by [80Yur] from the decomposition reaction  $TiN_{1-x} + 2BN = TiB_2 + \frac{x}{2} N_2$  was given as  $\Delta_f H(298) = -104667$  kJ/gratom and is slightly lower than the optimized value obtained from the modelling of the Ti-B binary (Table 2).

## MISCELLANEOUS

Fig.2 presents three isopleths  $TiB_2$ - $TiN_{1-x}$  for  $x=0.04$ , 0.27 and 0.42 after [81Chu] revealing the eutectic nature of the quasibinary section  $TiB_2$ -TiN and the increasing solubility of  $TiB_2$  in  $TiN_{1-x}$  with increasing  $x$  and temperature.

## REFERENCES

- [55Bre] L.Brewer and H.Haraldsen, "The Thermodynamic Stability of Refractory Metal Borides", J.Electrochem.Soc. 102 (1955) 399-406
- [61Now] H.Nowotny, F.Benesovsky, F.Brukl and O.Schob, "The Ternary Systems: Ti-B-C and Ti-B-N", Monatsh.Chemie 92 (1961) 403-414
- [66Rud] E.Rudy and S.Windisch "The System Ti-B " Techn.Rep. AFML-TR-65-2, Part I, Vol.VII, Wright Patterson Air Force Base, Oh, (1966)
- [70Car] J.O.Carlsson and T.Lundström, "The Solution Hardening of  $\beta$ -rhombohedral Boron", J.Less Common Met. 22 (1970) 317-320
- [72Med] O.A.Medvedeva, "Systems Metal-Boron-Nitrogen" (in Russian), Poroshkov.Metall. (2) (1972) 38-45
- [73Sam] G.V.Samsonov, A.L.Burykina, O.A.Medvedeva and V.P.Kosteruk, "Interaction of Boronnitride with Transition Metals, Their Borides and Nitrides" (in Russian), Poroshkov. Metall. (11) (1973) 50-57

- [76Fro] E.Fromm and E.Gebhardt, "Gases and Carbon in Metals" (in German), (Springer,Berlin,1976)
- [80Yur] T.J.Yurick and K.E.Spear, "Thermodynamics of  $TiB_2$  from Ti-B-N Studies", in "Thermodynamics of Nuclear Materials 1978", IAEA-SM-236/53 Vienna Vol I, (1980) 73-90
- [81Chu] V.D.Chupov, S.S.Ordan'yan and L.V.Kozlovskii, "Reaction in the  $TiN_x-TiB_2$  System", Inorganic Materials (English Transl.) 17 (1981) 1195-1198, translated from Izv.Akad.Nauk SSSR, Neorg.Mater.17 (1981) 1618-1622
- [83Tka] Yu.G.Tkachenko, S.S.Ordanyan D.Z.Yurchenko, V.K.Yulyugin and D.V.Chupov, "High Temperature Alloys in the Systems  $TiN_x-TiB_2$ " (in Russian), Poroshkov.Metall. (2) (1983) 70-76
- [84Bor] A.L.Borisova, Yu.S.Borisov, L.K.Chvedova and N.S.Marchenyuk, "Interaction in Powder Komponenten Ti-BN", (in Russian) Poroshkov.Metall. (4) (1984) 18-22
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, Oh, 1985)
- [86Len1] W.Lengauer, "The Crystal Structure of  $\eta-Ti_3N_2$  :An Additional New Phase in the Ti-N System", J.Less Common Met. 125 (1986) 127-134
- [86Len2] W.Lengauer and P.Ettmayer, "The Crystal Structure of a New Phase in the Titanium-Nitrogen System", J.Less Common Met. 120 (1986) 153-159
- [86Mur] J.L.Murray, P.K.Liao and K.E.Spear, " The B-Ti System ", Bull. Alloy Phase Diagrams 7 (1986) 550-555
- [87Len] W.Lengauer and P.Ettmayer, "Some Aspects of the Formation of  $\epsilon-Ti_2N$ ", Rev.Chim.Miner. 24 (1987) 707-713
- [87Šmi] I.Šmid and P.Rogl "Phase Relations in The Ternary System :Titanium - Boron - Nitrogen", research at the Univ. Vienna, (1987), to be published
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams" Amer.Soc.Met., Metals Park, Oh, 1988.
- [90Len] W.Lengauer, research at the Technical University of Vienna (1990) to be published

Table 1: Solid phases in the system B-Ti-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\beta$ -Ti 1663-882°	cI2 Im $\bar{3}$ m W	a= 330.65	[90Mas]
$\alpha$ -Ti <882 °	hP2 P6 <sub>3</sub> /mmc Mg	a= 295.06 c= 468.35	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.53 c=2381.03	[70Car]
		a=1092.70 c=2388.65	[70Car] at TiB <sub>x</sub>
TiB <2190°	oP8 Pbnn FeB	a= 456.01 b= 611.6 c= 305.65	[87 $\bar{S}$ mi]
Ti <sub>3</sub> B <sub>4</sub> <2200°	oI14 Imnn Ta <sub>3</sub> B <sub>4</sub>	a= 326.28 b=1373.5 c= 303.96	[87 $\bar{S}$ mi]
TiB <sub>2</sub> <3225°	hP3 P6/mnn AlB <sub>2</sub>	a= 303.56 c= 322.78	[87 $\bar{S}$ mi]
$\epsilon$ -Ti <sub>2</sub> N <1080°	tP6 P4 <sub>2</sub> /mnn TiO <sub>2</sub>	a= 494.28 c= 303.57	[85Vil] at 31 to 33 at% N [87Len]
$\eta$ -Ti <sub>3</sub> N <sub>2-x</sub> 1103-1066°	hR6 R $\bar{3}$ m VTa <sub>2</sub> C <sub>2</sub>	a= 297.95 c=2898.5	[86Len1] at 29 at% N
$\zeta$ -Ti <sub>4</sub> N <sub>3-x</sub> 1291-1076°	hR6 R $\bar{3}$ m V <sub>4</sub> C <sub>3</sub>	a= 296.09 c=2166.42	[86Len2] at 31.5 at% N

$\delta'$ -TiN <sub>1-x</sub> <800°	tI16 I4 <sub>1</sub> /amd ThSi <sub>2</sub> ?	a= 414.0 c= 880.5	[87Len] metastable at 38 at% N
TiN <sub>1-x</sub>	cF8 Fm $\bar{3}$ m NaCl	a= 423.9	[85Vil]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 888.1	[85Vil]

Table 2: Thermodynamic data for the system Ti-B-N

Phase	$\Delta_f G$ ( J/gramaton )	Ref.
1.0000 Ti	$\Delta_{fus} G(Ti) = 16234 - 8.368 T$	[86Mur]
1.0000 B	$\Delta_{fus} G(B) = 50210 - 21.23 T$	
1.0000 $\alpha$ Ti	$\Delta_f G(\alpha Ti) = 0$	
1.0000 $\beta$ Ti	$\Delta_f G(\beta Ti) = 4351 - 3.766 T$	
0.5000 TiB	$\Delta_f G(TiB) = -109721 + 13.23 T$	
0.1429 Ti <sub>3</sub> B <sub>4</sub>	$\Delta_f G(Ti_3B_4) = -114026 + 12.12 T$	
0.3333 TiB <sub>2</sub>	$\Delta_f G(TiB_2) = -106753 + 5.49 T$	
1.0000 $\beta$ B	$\Delta_f G(\beta B) = 0$	
Liquid	$\Delta G^{ex} = x(1-x)\{-272514 - 19.183 T + (-67899)(1-2x) + (-68144)(1-2x)^2 + (-38210)(1-2x)^3\}$	
0.5000 TiN	$\Delta_f G(TiN) = -167883 + 46.4424 T \quad (25^\circ < T < 882^\circ C)$ $-169138.2 + 47.4884 T \quad (882^\circ < T < 1200^\circ C)$	[76Fro]

Fig.1: Isothermal section at 1500°C in the system Ti - B - N under 1 bar Ar (in the absence of external nitrogen) [87Sm].

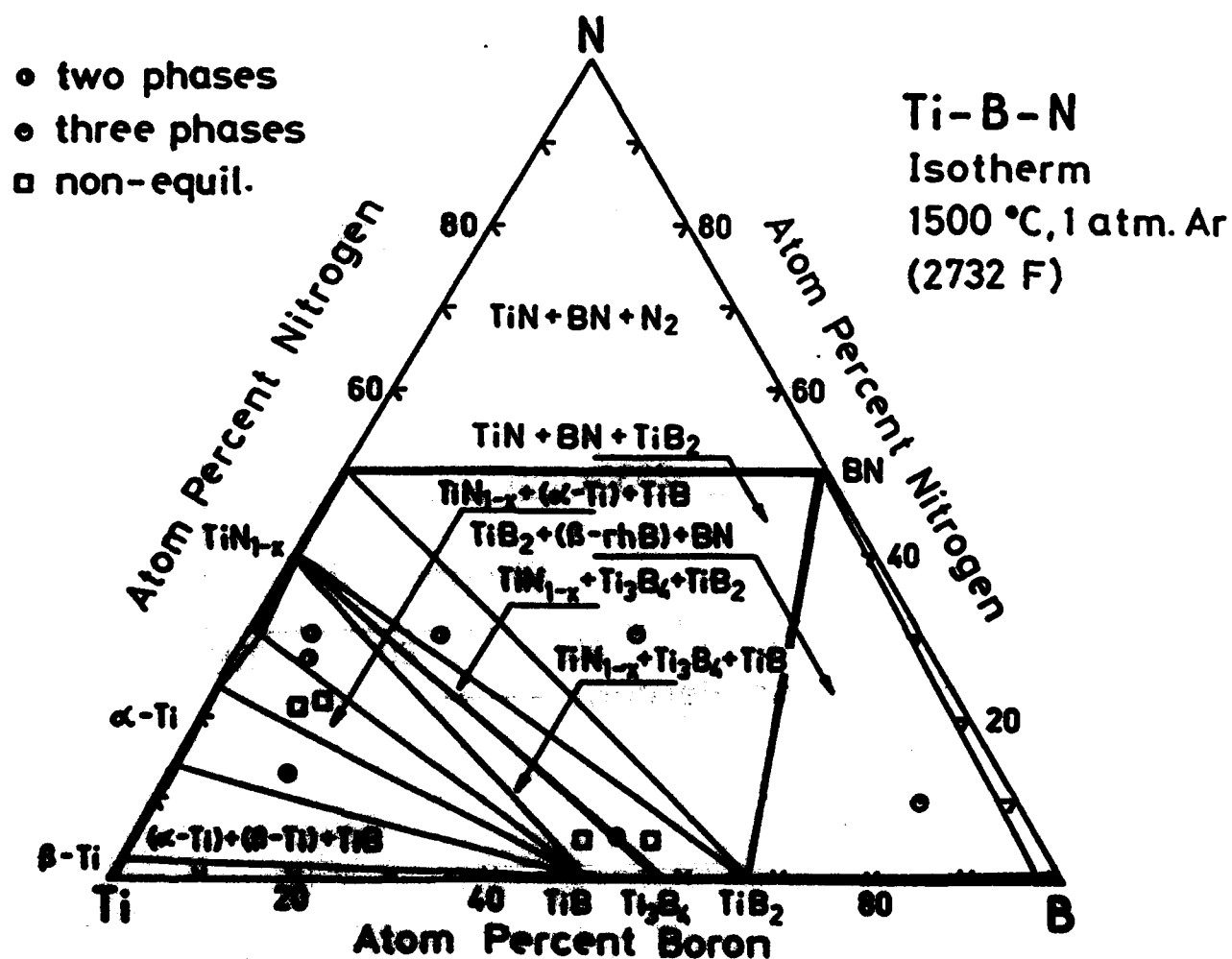
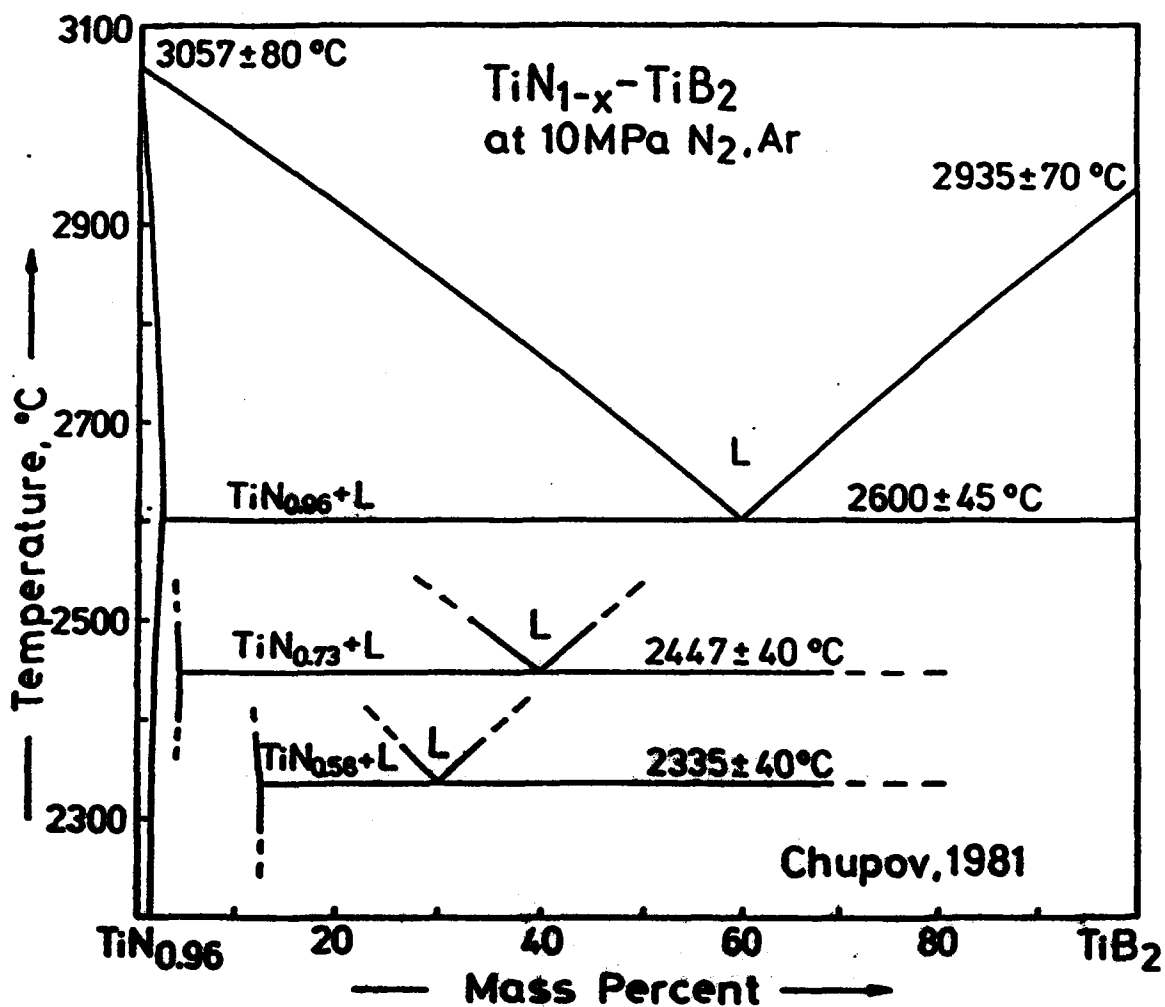


Fig.2: Comparison of the concentration sections  $\text{TiB}_2\text{-TiN}_{1-x}$  at  $x = 0.04, 0.27$  and  $0.42$  (based on [81Chu]).





## SYSTEM BORON - ZIRCONIUM - NITROGEN (B-Zr-N)

### INTRODUCTION / EXPERIMENTAL

Information on the Zr-B-N ternary are due to [55Bre, 61Rud, 73San, 74Spiv, 84Ord] and [87Smi] with an early review by [72Med].

Based on an early thermodynamic estimation of the reaction  $\text{ZrN} + 2 \text{BN} \rightleftharpoons \text{ZrB}_2 + \frac{3}{2} \text{N}_2$  under  $0.5 \cdot 10^5 \text{ Pa}$  of nitrogen, [55Bre] proposed stability of the mixture  $\text{ZrN} + \text{BN}$  up to ca  $1550^\circ\text{C}$ . Accordingly phase equilibria at  $1500^\circ\text{C}$  under argon of 0.1%  $\text{N}_2$  as derived by [61Rud] are characterized by the absence of ternary boronitride compounds and by a dominating three phase field  $\text{ZrB}_2 + \text{ZrN}_{1-x} + \text{BN}$ .

[84Ord] claimed the existence of a quasibinary section of the eutectic type  $\text{ZrB}_2 + \text{ZrN}$  revealing small mutual solid solubilities at the nitrogen-rich phase boundary  $\text{ZrN}_{0.98}$  (~2 mol%  $\text{ZrB}_2$  in  $\text{ZrN}_{0.98}$ ).

Phase equilibria in the B-Zr-N system have been corroborated by [87Smi] at  $1500^\circ$  under high vacuum or 1 bar Ar or under 1 bar  $\text{N}_2$  respectively. Phase relations have been established from room temperature X-ray powder diffraction analysis of about 10 binary and 25 ternary samples prepared by reaction sintering of cold compacted powder blends of B, BN, Zr, ZrN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than  $20 \mu\text{m}$  in a steel mortar and/or a WC-Co mortar respectively [87Smi]. For annealing in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N- $\text{N}_2$ ) the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments usually consisted of a primary reaction at  $1500^\circ\text{C}$  for 72h followed by a final reaction at  $1500^\circ\text{C}$  up to 144h with an intermediate step of crushing and recompacting to ensure homogeneity. After heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Zr, crystallized boron (99.8 % B),  $\text{ZrN}_{1-x}$  (99.8%) and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at  $1400^\circ\text{C}$ . Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [87Smi].

## BINARY SYSTEMS

The reinvestigation [87<sup>X</sup>Smi] of the B-Zr system in the range from 900 to 2400°C revealed consistency with the data available in [84Vil], and [90Mas]; a critical assessment is due to [88Rog]. The maximal solid solubility of boron in zirconium was claimed to be less than 1 at%B at 1680°C [88Rud] and an interstitial type of B-solubility was suggested. The maximum solid solubility of Zr in  $\beta$ -B was reported to be less than 0.5 at% Zr at ~1800°C from X-ray powder data [81Cre] (see Table 1). Fig.1 is a representation of the constitutional diagram Zr-B.

The phase diagram for the system Zr-N is in accordance with [90Mas]. Crystallographic information on the binary zirconium compounds is found in Table 1.

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.2 summarizes the results on the phase relations at 1500°C under 1 bar Ar as observed by [61Rud] and confirmed by [87<sup>X</sup>Smi]. Phase equilibria are characterized by the absence of ternary compounds and by incompatibility of zirconium metal and  $\text{BN}_{\text{hex}}$  due to the formation of a stable tie line  $\text{ZrB} - \text{ZrN}_{1-x}$  at temperatures below 1500°C. Heating binary as well as ternary alloys at 1500°C under 1 bar  $\text{N}_2$  transfers all samples to the limiting tie line at the nitrogen rich boundary  $\text{ZrN} + \text{BN}$ , equilibrium being reached after 75h of nitrogen exposure.

As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Zr in BN up to 1500°C. There is furthermore no solubility of N in  $\text{ZrB}_2$ , whereas the solubility of zirconium boride in the zirconium nitride at 1500°C was observed to be rather extended [61Rud, 87<sup>X</sup>Smi], see also Fig.2.

## THERMODYNAMICS

A thermodynamic modelling of the binary system Zr-B is due to [88Rog]; see Table 2. For the calculation of the Zr-B-N phase equilibria see [55Bre].

## MISCELLANEOUS

Fig.3 presents the isopleth  $\text{ZrB}_2\text{-ZrN}_{1-x}$  for  $x=0.04$  after [84Ord] revealing the eutectic nature of the quasibinary. Microhardness and creep rate of  $\text{ZrB}_2\text{-ZrN}$  composites have been studied by [74Spi].

## REFERENCES

- [55Bre] L.Brewer and H.Haraldsen, "The Thermodynamic Stability of Refractory Metal Borides", J.Electrochem.Soc. 102 (1955) 399-408
- [61Rud] E.Rudy and F.Benesovsky, "Investigations in the Systems: Hf-B-N and Zr-B-N", Monatsh.Chemie 92 (1961) 415-441
- [72Med] O.A.Medvedeva, "Systems Metal-Boron-Nitrogen" (in Russian), Poroshkov.Metall. (2) (1972) 38-45
- [73San] G.V.Samsonov, A.L.Burykina, O.A.Medvedeva and V.P.Kosteruk, "Interaction of Boronnitride with Transition Metals, Their Borides and Nitrides" (in Russian), Poroshkov. Metall. (11) (1973) 50-57
- [74Spi] I.I.Spivak, R.A.Andrievsky, V.V.Klinenko and V.D.Lazarenko, "Investigations of Creeping in Binary Systems  $\text{TiB}_2\text{-TiC}$ ,  $\text{ZrB}_2\text{-ZrN}$ ", Poroshkov.Metallurg.140 (1974) 17-21
- [76Fro] E.Fromm and E.Gebhardt, "Gases and Carbon in Metals" (in German), (Springer,Berlin,1978)
- [78Cal] B.Callmer, L.E.Tergenius and J.O.Thomas, "X-ray Powder Profile Refinement of Zirconium in  $\beta$ -rh.Boron", J.Solid State Chem. 26 (1978) 275-279
- [81Cre] A.J.Crespo, L.E.Tergenius and T.Lundström, "The Solution of 4d, 5d and some p Elements in  $\beta$  rhombohedral Boron", J.Less-Common Met. 77 (1981) 147-150
- [84Ord] S.S.Ordanyan and V.D.Chupov, "Interaction in  $\text{ZrN-ZrB}_2$  and  $\text{HfN-HfB}_2$  Systems", Inorg.Mater (Engl.Transl.) 20 (1984) 1719-1722 translated from Izv.Akad.Nauk SSSR,Neorg.Mater. 20 (1984) 1979-1982
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met.,Metals Park,Oh, 1985)

- [87<sup>Y</sup>Sm] I. Smid and P. Rogl "Phase Relations in The Ternary System :Zirconium-Boron-Nitrogen", research at the Univ. Vienna, (1987), to be published
- [88Rog] P. Rogl and P.E. Potter, "A Critical Review and Thermodynamic Calculation of The Binary System Zr-B", Calphad 12 (1988) 191-204
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., Amer. Soc. Met., Metals Park, Oh, 1990

Table 1: Solid phases in the system B-Zr-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\beta$ -Zr 1855-863°	cI2 Im $\bar{3}m$ W	a= 360.90	[90Mas]
$\alpha$ -Zr <863 °	hP2 P6 <sub>3</sub> /mmc Mg	a= 323.16 c= 514.75	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}m$ $\beta$ -B	a=1092.76 c=2381.41	[81Cre]
		a=1095.64 c=24.0201	[78Car] at ZrB <sub>54</sub>
ZrB <sub>2</sub> <3245°	hP3 P6/mmm AlB <sub>2</sub>	a= 316.94 c= 353.03 a= 316.92 c= 353.09	[82Lei] Zr-rich [82Lei] B- rich
ZrB <sub>12</sub> 2250-1710°	cF52 Fm $\bar{3}m$ UB <sub>12</sub>	a= 740.8	[85Vil]
ZrN <sub>1-x</sub>	cF8 Fm $\bar{3}m$ NaCl	a= 458.5	[85Vil]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]

Table 2: Thermodynamic data for the system Zr-B-N

Phase	$\Delta_f G$ ( J/granaton )	Ref.
1.0000 Zr	$\Delta_{fus} G(Zr) = 21000 - 9.868 T$	[88Rog]
1.0000 B	$\Delta_{fus} G(B) = 50210 - 21.23 T$	
1.0000 $\alpha Zr$	$\Delta_f G(\alpha Zr) = 0$	
1.0000 $\beta Zr$	$\Delta_f G(\beta Zr) = 4103.3 - 3.601 T$	
0.3333 $ZrB_2$	$\Delta_f G(ZrB_2) = -108600 + 4.98 T$	
0.0769 $ZrB_{12}$	$\Delta_f G(ZrB_{12}) = -20200 - 1.93 T$	
1.0000 $\beta B$	$\Delta_f G(\beta B) = 0$	
Liquid(Zr,B)	$\Delta G^{ex} = x(1-x)\{-185408 - 16.03 T + (66465)(1-2x) + (13412)(1-2x)^2\}$	
0.5000 ZrN	$\Delta_f G(ZrN) = -183230 + 48.325 T$	[76Fro]

Fig.1: The binary system Zr - B; based on [90Mas] and [87Sni].

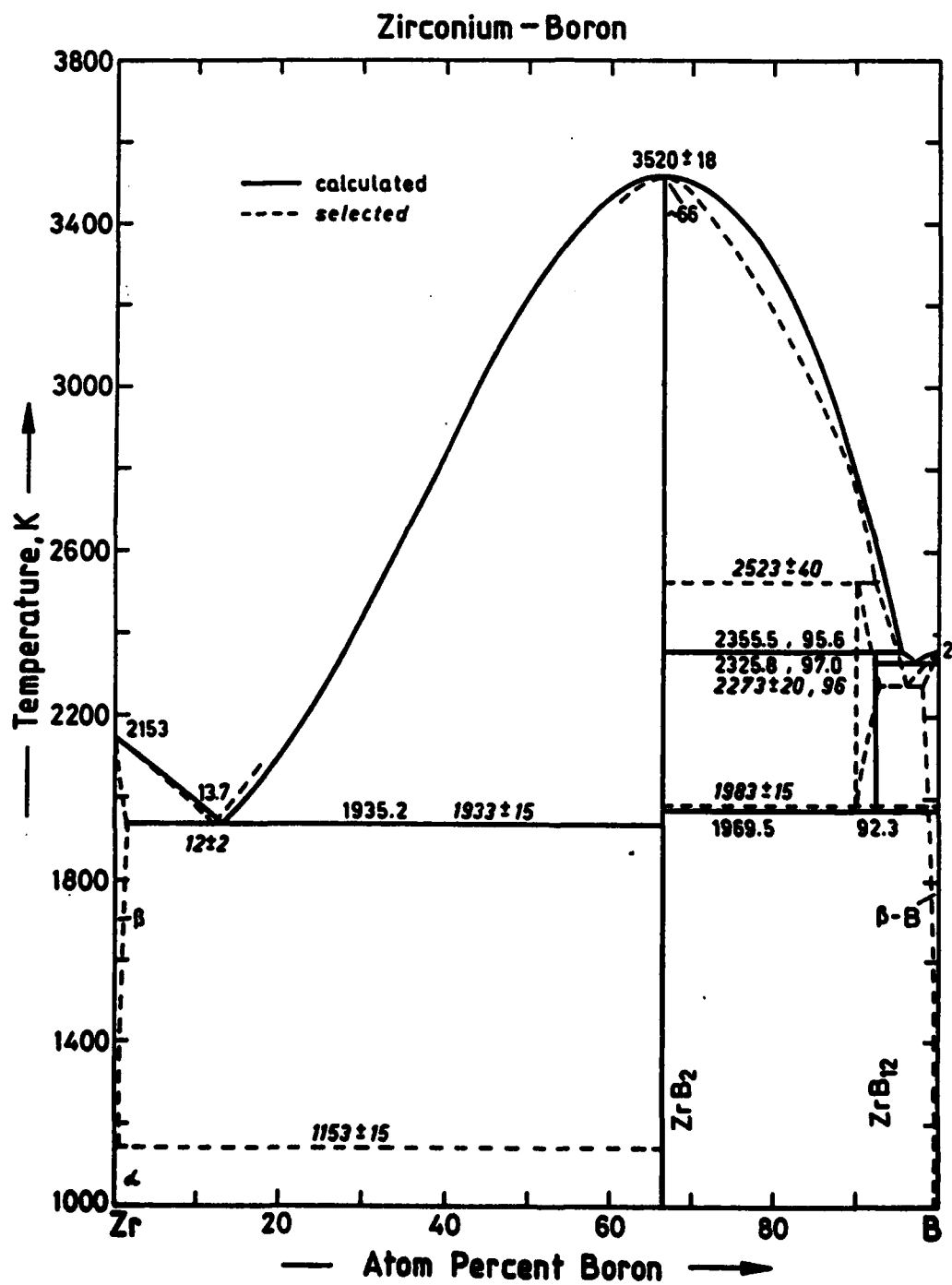


Fig.2: Isothermal section at 1500°C in the system Zr - B - N  
under 1 bar Ar (in the absence of external nitrogen) [87<sup>Y</sup>Si].

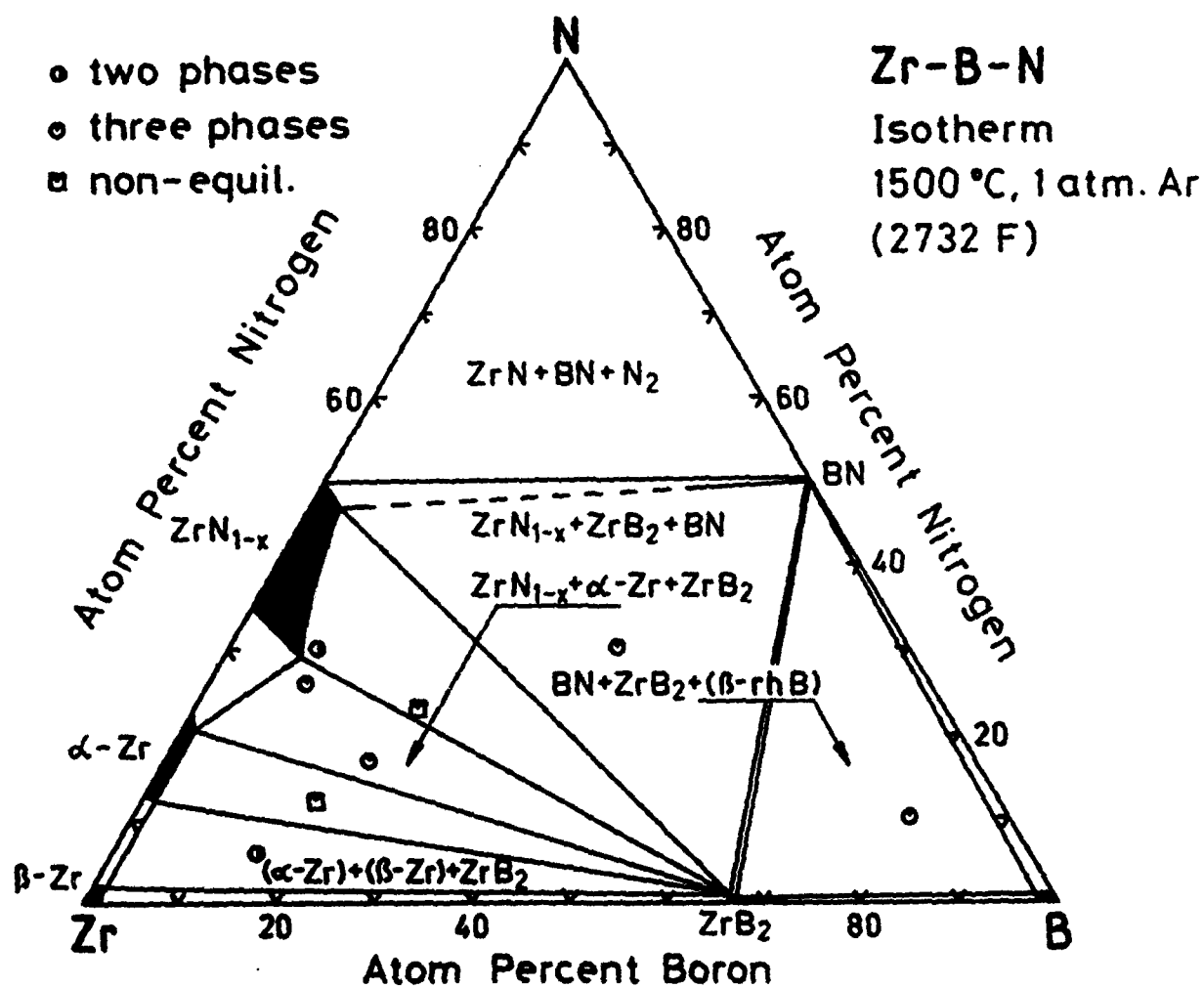
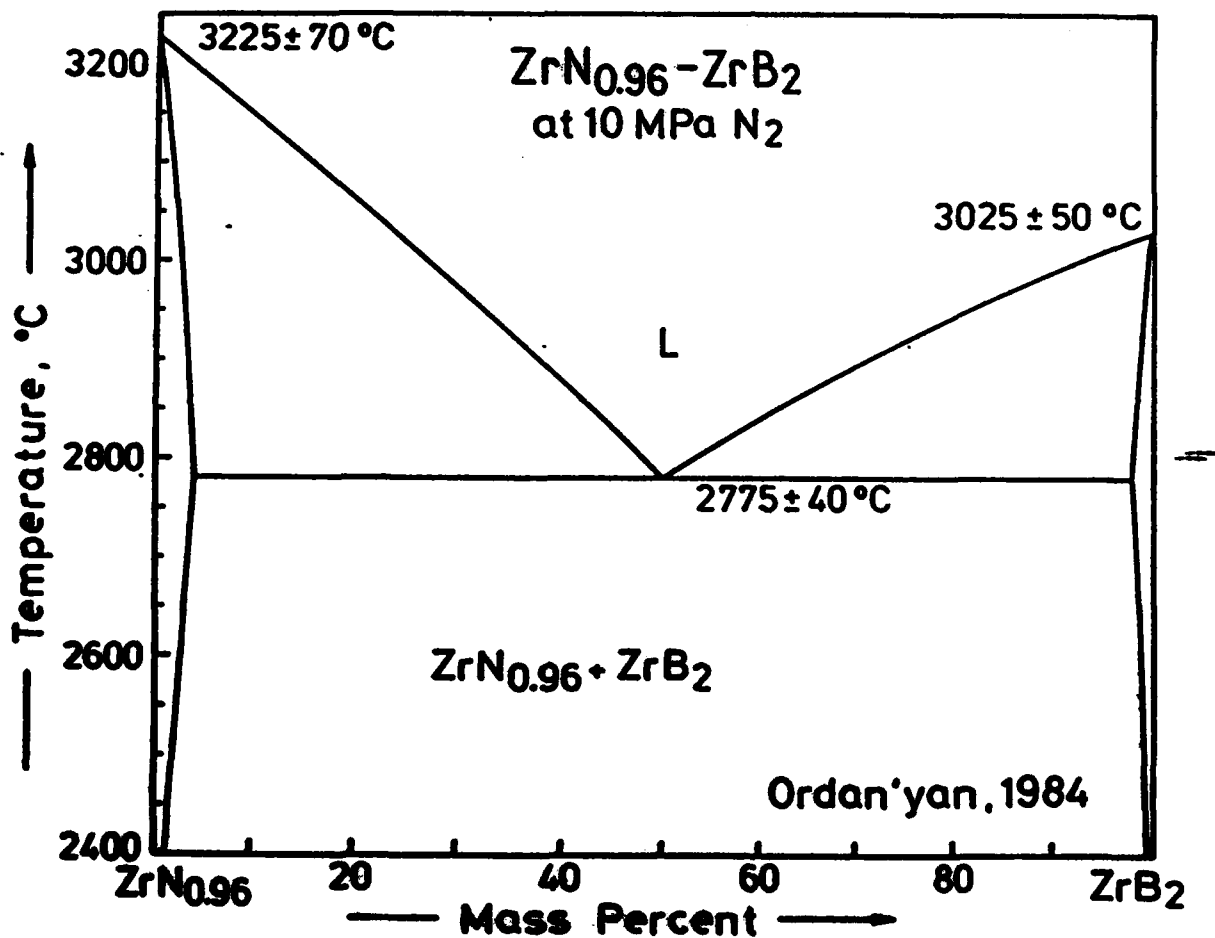




Fig.3: The concentration section  $\text{ZrB}_2\text{-ZrN}_{1-x}$  at  $x = 0.04$   
(based on [84Ord]).



## SYSTEM BORON - HAFNIUM - NITROGEN (B-Hf-N)

### INTRODUCTION / EXPERIMENTAL

Informations on the Hf-B-N ternary are due to [81Rud, 73San, 84Ord] and [87<sup>X</sup>Smi] with an early review by [72Med].

Phase equilibria at 1500°C under argon of 0.1% N<sub>2</sub> as derived by [81Rud] are characterized by the absence of ternary boronitride compounds and by a dominating three phase field  $\text{HfB}_2 + \text{HfN}_{1-x} + \text{BN}$ .

[84Ord] claimed the existence of a quasibinary section of the eutectic type  $\text{HfB}_2 + \text{HfN}$  revealing small mutual solid solubilities at the nitrogen-rich phase boundary  $\text{HfN}_{0.97}$  (~2 mol%  $\text{HfB}_2$  in  $\text{HfN}_{0.97}$ ).

Phase equilibria in the B-Hf-N system have been corroborated by [87<sup>X</sup>Smi] at 1500° under high vacuum or 1 bar Ar or under 1 bar N<sub>2</sub> respectively. Phase relations have been established from room temperature X-ray powder diffraction analysis of about 10 binary and 25 ternary samples prepared by reaction sintering of cold compacted powder blends of B, BN, Hf, HfN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20µm in a steel mortar and/or a WC-Co mortar respectively [87<sup>X</sup>Smi]. For annealing in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N<sub>2</sub>) the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments usually consisted of a primary reaction at 1500°C for 72h followed by a final reaction at 1500°C up to 144h with an intermediate step of crushing and recompacting to ensure homogeneity. After heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Hf, crystallized boron (99.8 % B),  $\text{HfN}_{1-x}$  (99.8%) and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [87<sup>X</sup>Smi].

### BINARY SYSTEMS

The reinvestigation [87<sup>X</sup>Smi] of the B-Hf system in the range from

900 to 2400°C revealed consistency with the data available in [84Vil], and [90Mas]; a critical assessment is due to [88Rog]. The maximal solid solubility of boron in hafnium was claimed to be less than 2 at%B at 1880°C [88Rud] and an interstitial type of B-solubility was suggested. The maximum solid solubility of Hf in  $\beta$ -B was reported to be less than 0.5 at% Hf at ~1800°C from X-ray powder data [81Cre] (see Table 1). Fig.1 is a representation of the constitutional diagram Hf-B.

A critical assessment of the phase diagram for the system Hf-N is due to [90Ka]

Crystallographic information on the binary hafnium compounds is found in Table 1.

#### SOLID PHASES / ISOTHERMAL SECTIONS

Fig.2 summarizes the results on the phase relations at 1500°C under 1 bar Ar as observed by [81Rud] and confirmed by [87<sup>V</sup>Si]. Phase equilibria are characterized by the absence of ternary compounds and by incompatibility of hafnium metal and  $\text{BN}_{\text{hex}}$  due to the formation of a stable tie line  $\text{HfB} - \text{HfN}_{1-x}$  at temperatures below 1500°C. Heating binary as well as ternary alloys at 1500°C under 1 bar  $\text{N}_2$  transfers all samples to the limiting tie line at the nitrogen rich boundary  $\text{HfN} + \text{BN}$ , equilibrium being reached after 75h of nitrogen exposure.

As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Hf in BN up to 1500°C. There is furthermore no solubility of N in  $\text{HfB}_2$ , whereas the solubility of hafniumboride in hafniumnitride at 1500°C was observed to be rather extended [81Rud, 87<sup>V</sup>Si], see also Fig.2.

#### THERMODYNAMICS

A thermodynamic modelling of the binary system Hf-B is due to [88Rog]; see Table 2. The thermodynamic data available are consistent with the ternary phase equilibria experimentally observed.

#### MISCELLANEOUS

Fig.3 represents the isopleth  $\text{HfB}_2 - \text{HfN}_{1-x}$  for  $x=0.03$  after [84Ord] revealing the eutectic nature of the quasibinary.

## REFERENCES

- [61Rud] E.Rudy and F.Benesovsky, "Investigations in the Systems: Hf-B-N and Zr-B-N", *Monatsh.Chemie* 92 (1961) 415-441
- [72Med] O.A.Medvedeva, "Systems Metal-Boron-Nitrogen" (in Russian), *Poroshkov.Metall.* (2) (1972) 38-45
- [73San] G.V.Samsonov, A.L.Burykina, O.A.Medvedeva and V.P.Kosteruk, "Interaction of Boronnitride with Transition Metals, Their Borides and Nitrides" (in Russian), *Poroshkov. Metall.* (11) (1973) 50-57
- [76Fro] E.Fromm and E.Gebhardt, "Gases and Carbon in Metals", (Springer, Berlin, 1976)
- [81Cre] A.J.Crespo, L.E.Tergenius and T.Lundström, "The Solution of 4d, 5d and some p Elements in  $\beta$  rhombohedral Boron", *J.Less-Common Met.* 77 (1981) 147-150
- [84Ord] S.S.Ordanyan and V.D.Chupov, "Interaction in ZrN-ZrB<sub>2</sub> and HfN-HfB<sub>2</sub> Systems", *Inorg.Mater (Engl.Transl.)* 20 (1984) 1719-1722 translated from *Izv.Akad.Nauk SSSR, Neorg.Mater.* 20 (1984) 1979-1982
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, Oh, 1985)
- [87Šmi] I.Šmid and P.Rogl "Phase Relations in The Ternary System :Hafnium - Boron - Nitrogen", research at the Univ. Vienna, (1987), to be published
- [88Rog] P.Rogl and P.E.Potter, "A Critical Review and Thermodynamic Calculation of The Binary System Hf-B", *Calphad* 12 (1988) 207-218
- [90Mas] T B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., Amer.Soc.Met., Metals Park, Oh, 1990.

Table 1: Solid phases in the system B-Hf-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\beta$ -Hf 2227-1743°	cI2 Im $\bar{3}m$ W	a= 361.0	[90Mas]
$\alpha$ -Hf <1743°	hP2 P6 <sub>3</sub> /mmc Mg	a= 319.46 c= 505.10	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}m$ $\beta$ -B	a=1092.76 c=2381.41	[81Cre]
HfB <2100°	oP8 Pbnm FeB	a= 492.38 b= 652.4 c= 322.35	[87 <sup>V</sup> Si]
HfB <sub>2</sub> <3380°	hP3 P6/mmm AlB <sub>2</sub>	a= 314.28 c= 347.89 a= 314.31 c= 347.80	[87 <sup>V</sup> Si] Hf-rich [87 <sup>V</sup> Si] B- rich
Hf <sub>3</sub> N <sub>2</sub> <1970°	hR6 R $\bar{3}m$ VTa <sub>2</sub> C <sub>2</sub>	a= 320.6 c=2328.	[85Vil]
Hf <sub>4</sub> N <sub>3</sub> <2300°	hR8 R $\bar{3}m$ V <sub>4</sub> C <sub>3</sub>	a= 321.4 c=3112	[85Vil]
HfN <sub>1-x</sub>	cF8 Fm $\bar{3}m$ NaCl	a= 451.18	[85Vil]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 888.1	[85Vil]

Table 2: Thermodynamic data for the system Hf-B-N

Phase	$\Delta_f G$ ( J/gramatom )	Ref.
1.0000 Hf	$\Delta_{fus} G(\text{Hf}) = 27198 - 10.861 T$	[88Rog]
1.0000 B	$\Delta_{fus} G(\text{B}) = 50210 - 21.23 T$	
1.0000 $\alpha\text{Hf}$	$\Delta_f G(\alpha\text{Hf}) = 0$	
1.0000 $\beta\text{Hf}$	$\Delta_f G(\beta\text{Hf}) = 5860.3 - 2.907 T$	
0.5000 HfB	$\Delta_f G(\text{HfB}) = -98800 - 6.30 T$	
0.3333 HfB <sub>2</sub>	$\Delta_f G(\text{HfB}_2) = -109500 + 4.13 T$	
1.0000 $\beta\text{B}$	$\Delta_f G(\beta\text{B}) = 0$	
Liquid(Hf,B)	$\Delta G^{ex} = x(1-x)\{-157123 - 17.19 T + (36259 + 8.666 T)(1-2x) + (2487)(1-2x)^2\}$	
0.5000 HfN	$\Delta_f G(\text{HfN}) = -1845105 + 42.48 T$	[76Fro]

Fig.1: The binary system Hf - B; based on [900ka] and [87Sm1].

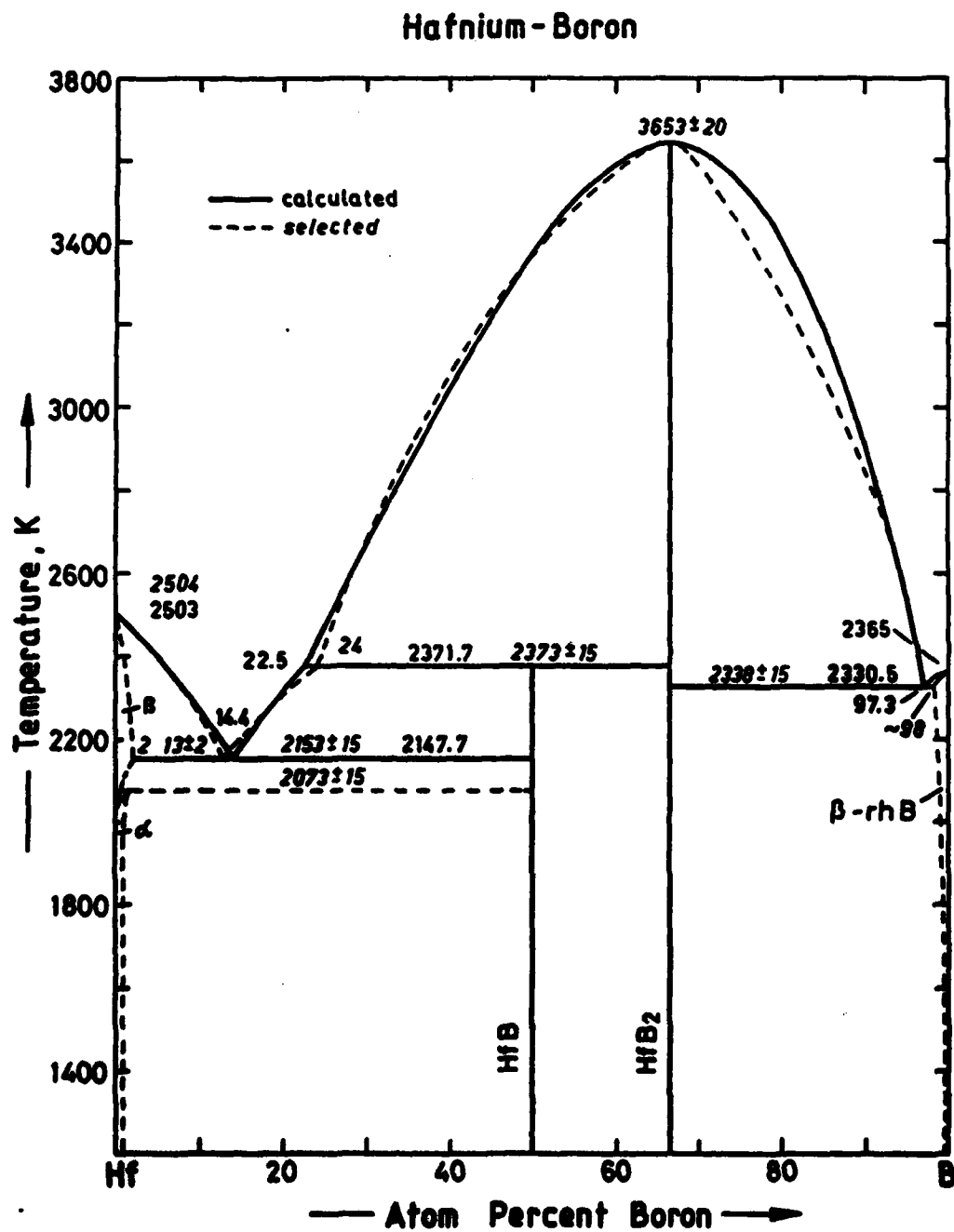


Fig.2: Isothermal section at 1500°C in the system Hf - B - N under 1 bar Ar (in the absence of external nitrogen) [87<sup>Smi</sup>].

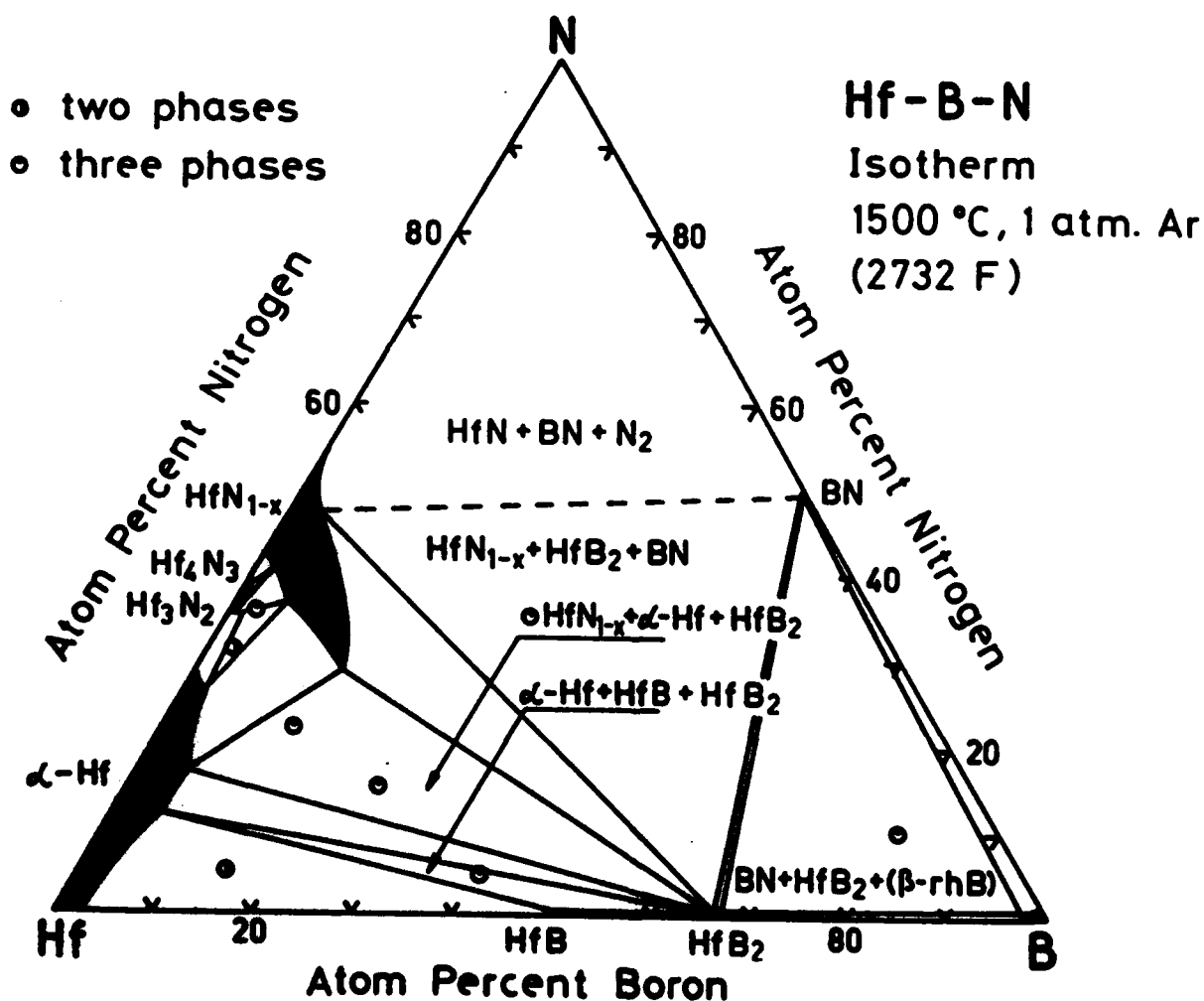
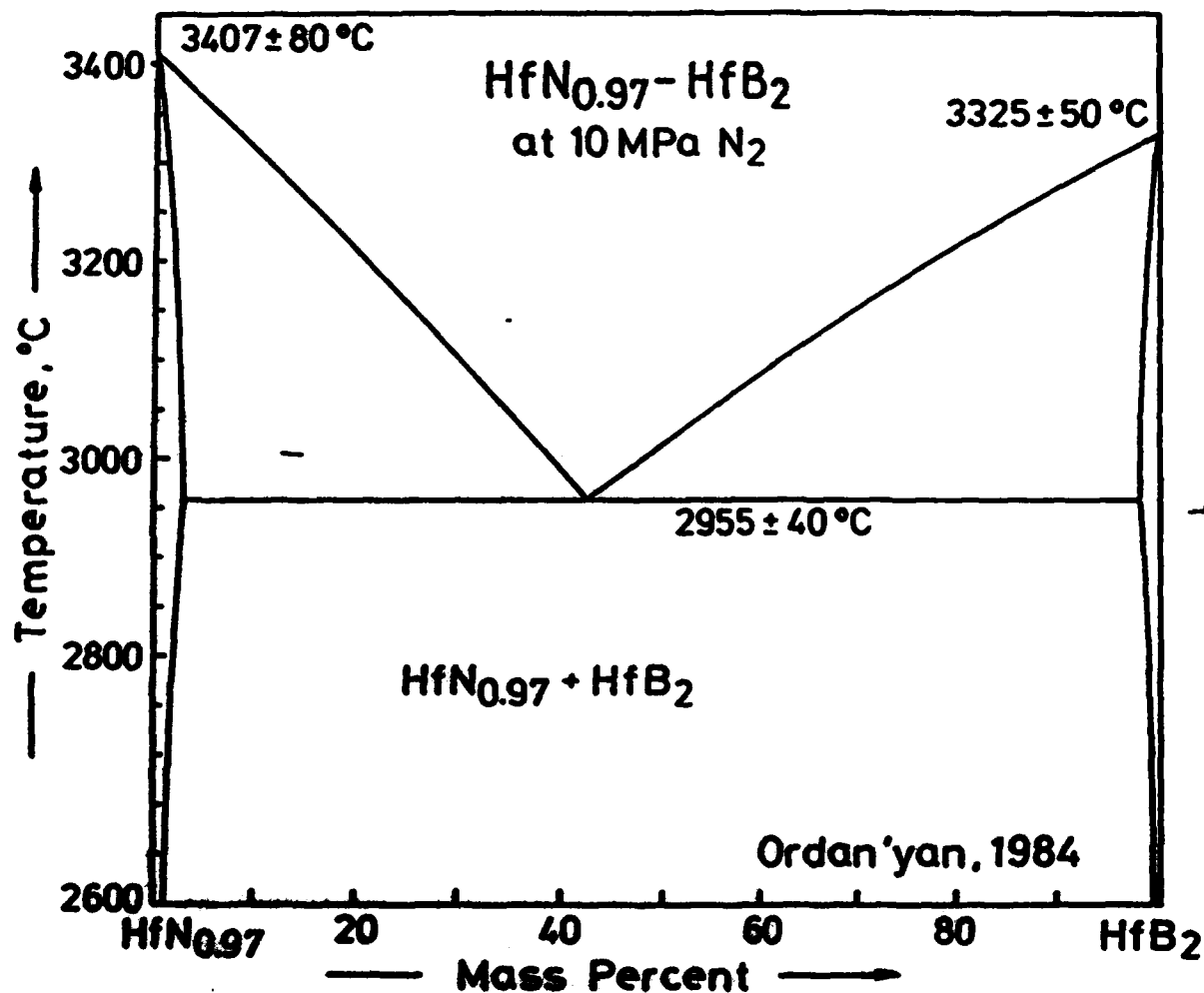




Fig.3: The concentration section  $\text{HfB}_2$ - $\text{HfN}_{0.97}$  at  $x = 0.93$   
(based on [84Ord]).



## SYSTEM BORON- VANADIUM - NITROGEN (B-V-N)

### INTRODUCTION / EXPERIMENTAL

Informations on the V-B-N ternary are due to [88Spe] and [89Rem].

[88Spe] reported phase equilibria under 1 bar of nitrogen and listed the temperatures at which three solid phases are in equilibrium with the gas phase:



No details were given for the region  $\text{V} + \text{VN}_{1-x} + \text{VB}$ , however,  $\text{V}_2\text{B}_3$  was said to react with  $\text{V}_2\text{N}_{1-x}$  under 1 bar  $\text{N}_2$  below ca 2010 K to  $\text{VN}_{1-x} + \text{BN}$  [88Spe] (see also Fig.1).

Phase equilibria in the B-V-N system have been furthermore investigated [89Rem] at 1200° under high vacuum or 1 bar Ar or under 1 bar  $\text{N}_2$  respectively. Phase relations have been established from room temperature X-ray powder diffraction analysis of about 20 binary and 25 ternary samples prepared by reaction sintering of cold compacted powder blends of B, BN, V, VN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20µm in a steel mortar and/or a WC-Co mortar respectively [89Rem]. For annealing in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N- $\text{N}_2$ ) the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments usually consisted of a primary reaction at 1200°C for 72h followed by a final reaction at 1200°C up to 144h with an intermediate step of crushing and recompacting to ensure homogeneity. After heat treatment all samples were radiation cooled. Starting materials were powders of 3N-V, crystallized boron (99.8 % B),  $\text{VN}_{1-x}$  (99.8%) and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [89Rem].

## BINARY SYSTEMS

The reinvestigation [89Rem] of the B-V system in the range from 900 to 1800°C revealed consistency with the data available in [84Vil], and [90Mas]; a critical assessment is due to [87Spe]. The maximal solid solubility of boron in vanadium was claimed to be less than 1 at%B at 1737°C [86Rud] ; an interstitial type of B-solubility was suggested. The maximum solid solubility of V in  $\beta$ -B was reported to be less than 1 at% V at ~1800°C from X-ray single crystal data obtained on VB<sub>85</sub> and VB<sub>185</sub> by [86Gar] (see Table 1). Fig.1 is a representation of the constitutional diagram V-B.

The phase diagram for the system V-N is taken from [90Mas] modified according to [78Ono,82Ono] regarding the various ordered structures occurring within the homogeneity range of  $\beta$ -V<sub>2</sub>N<sub>1-x</sub> ( see Table 1 ) A detailed discussion of solubility data , physical properties and thermodynamic data is found in [76Fro].

Crystallographic information on the binary vanadium compounds is found in Table 1.

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.2 summarizes the results on the phase relations under 1 bar N<sub>2</sub> as observed by [88Spe].

Figs.3,4 represent the isothermal sections at 1200°C under 1 bar Ar and under 1 bar of N<sub>2</sub> respectively [89Rem]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between the higher vanadium borides and BN. Vanadium metal is not compatible with BN<sub>hex</sub> due to the formation of a stable tie line VB - VN<sub>1-x</sub> at temperatures below 1750°C. Heating binary as well as ternary alloys at 1200°C under 1 bar N<sub>2</sub> transfers all samples to the limiting tie line at the nitrogen rich boundary VN + BN, equilibrium being reached after 75h of nitrogen exposure (Fig.3, [89Rem]).

As seen from a comparison of the unit cell dimensions there is no significant solid solubility of V in BN up to 1800°C, and mutual solubilities of the vanadium borides, the vanadium nitrides and BN up to 1200°C are rather restricted [89Rem].

## THERMODYNAMICS

A thermodynamic modelling of the binary system V-B is due to [87Spe]; see Table 2.

## REFERENCES

- [86Rud] E. Rudy and S. Windisch "The System V-B " Techn. Rep. AFML-TR-85-2, Part I, Vol X, Wright Patterson Air Force Base, Oh, (1986)
- [76Fro] E. Fromm, and E. Gebhardt, "Gases and Carbon in Metals" (Springer, Berlin, 1976)
- [78Ono] T. Onozuka, " Vacancy Ordering in  $VN_{1-x}$  ", J. Appl. Crystallogr. 11 (1978) 132-136
- [82Ono] T. Onozuka, " Nitrogen Ordering in  $V_8N_4$  and  $V_{32}N_{20}$  Studied by Neutron and Electron Diffraction ", Trans. Jap. Inst. Metals 23 (1982) 315-319
- [82Pom] R. Pompe, "Some Thermodynamic Properties of the System V-N and V-C-N in the Temperature Range 1000 to 1550°C", Thermochem. Acta 57 (1982) 273-281
- [85Vil] P. Villars and L. D. Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, Oh, 1985)
- [88Gar] M. F. Garbouskas, J. S. Kasper and G. A. Slack, "The Incorporation of Vanadium in  $\beta$ -Boron as Determined by Single Crystal Diffractometry", J. Solid State Chem 63 (1986) 424-430
- [87Spe] K. E. Spear, P. K. Liao and J. F. Smith, " The B-V System ", Bull. Alloy Phase Diagrams 8 (1987) 447-454
- [89Rem] K. Renschnig and P. Rogl "Phase Relations in The Ternary System :Vanadium - Boron - Nitrogen", research at the Univ. Vienna, (1989) ,to be published
- [90Mas] T. B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., Amer. Soc. Met., Metals Park, Oh, 1990.

Table 1: Solid phases in the system B-V-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
V <1910°	cI2 Im $\bar{3}$ m W	a= 302.40	[80Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
		a=1097.2 c=2390.8	[86Gar] at VB $_{\infty}$
		a=1094.9 c=2384.0	[86Gar] at VB $_{105}$
V $_5$ B $_2$ <1900°	tP10 P4/nbm U $_5$ Si $_2$	a= 574.14 c= 302.95	[89Ren]
VB <2570°	oC8 Cmcm CrB	a= 308.03 b= 805.40 c= 297.20	[89Ren]
V $_5$ B $_6$ <1750°	oC22 Cmnn V $_5$ B $_6$	a= 297.84 b=2130.8 c= 305.85	[89Ren]
V $_5$ B $_4$ <2610°	oI14 Imnn Ta $_5$ B $_4$	a= 308.06 b=1322.0 c= 298.10	[89Ren]
V $_2$ B $_9$ <2670°	oC20 Cmcm V $_2$ B $_9$	a= 305.88 b=1842.2 c= 298.48	[89Ren]
VB $_2$ <2747°	hP3 P6/mmm AlB $_2$	a= 299.89 c= 305.80	[89Ren]
V $_2$ N $_4$	hP* P6 $_3$ 22 V $_2$ N $_4$	a= 491.0 c= 455.	[82Ono]

$V_2N$	hP9	a= 491.7	[85Vil]
	P6 <sub>2</sub> 22	c= 456.8	
	Mn <sub>2</sub> N <sub>0.88</sub>		
$V_{22}N_{20}$ <520°	tP58	a=2α(VN)	[78Ono]
	P4 <sub>2</sub> /nmc	c=2α(VN)	
	V <sub>22</sub> N <sub>20</sub>		
VN <sub>1-x</sub>	cF8	a= 413.6	[85Vil]
	Fm $\bar{3}$ m		
	NaCl		
BN <sub>hex</sub>	hP*	a= 250.4	[85Vil]
	P6 <sub>2</sub> /nmc	c= 866.1	
	BN <sub>hex</sub>		

Table 2: Thermodynamic data for the system V-B-N

Phase	$\Delta_f G$ ( J/gramatom )	Ref.
1.0000 V	$\Delta_{fus} G(V) = 20950 - 9.63 T$	[87Spe]
1.0000 B	$\Delta_{fus} G(B) = 50210 - 21.23 T$	
1.0000 V	$\Delta_f G (V) = 0$	
0.4000 V <sub>2</sub> B <sub>2</sub>	$\Delta_f G (V_2B_2) = -58070 + 1.67 T$	[76Fro]
0.5000 VB	$\Delta_f G (VB) = -69134 + 2.51 T$	
0.5450 V <sub>5</sub> B <sub>6</sub>	$\Delta_f G (V_5B_6) = -70116 + 2.85 T$	
0.5710 V <sub>5</sub> B <sub>4</sub>	$\Delta_f G (V_5B_4) = -70290 + 2.85 T$	
0.6000 V <sub>2</sub> B <sub>3</sub>	$\Delta_f G (V_2B_3) = -69856 + 3.05 T$	
0.3333 VB <sub>2</sub>	$\Delta_f G (VB_2) = -67853 + 3.35 T$	
1.0000 $\beta B$	$\Delta_f G (\beta B) = 0$	
Liquid(V,B)	$\Delta G^{ex} = x(1-x)\{-186352 + 12.55 T + (107479 - 43.82 T)(1-2x) + 57516(1-2x)^2\}$	
0.3431 V <sub>2</sub> N <sub>0.88</sub>	$\Delta_f G (V_2N_{0.88}) = -89591 + 30.55 T$	[82Pom]
0.5000 VN <sub>1-x</sub>	$\Delta_f G (VN_{1-x}) = -77404 + 46.024 T$	

Fig.1: The binary system V - B; based on [65Rud, 86Mas] and [89Rem].

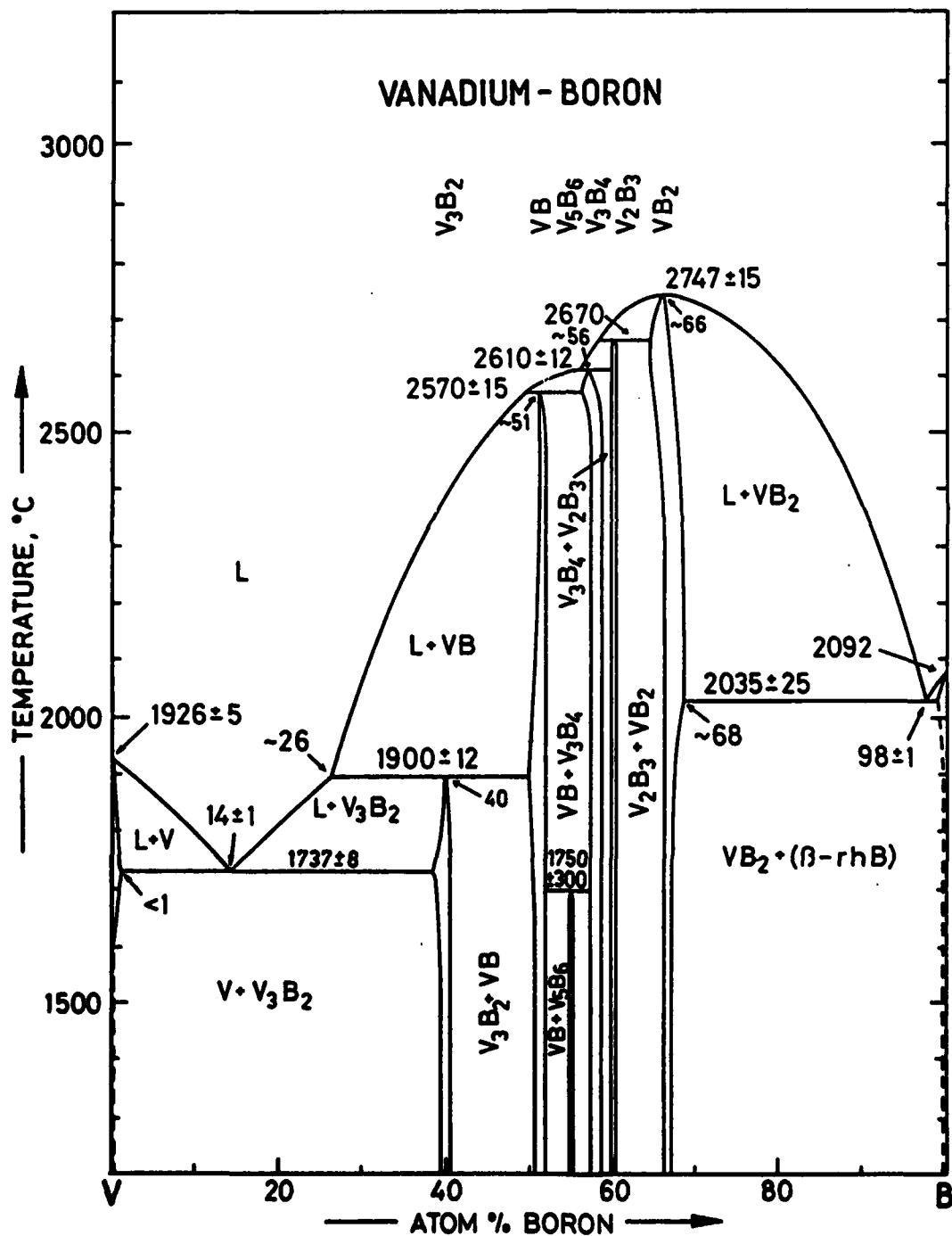


Fig.2: Phase relations in the system V - B - N  
under 1 bar  $N_2$  ( after [68Spe] ), the temperatures listed  
refer to the maximal temperatures under which three solid  
phases are stable under 1 bar  $N_2$ .

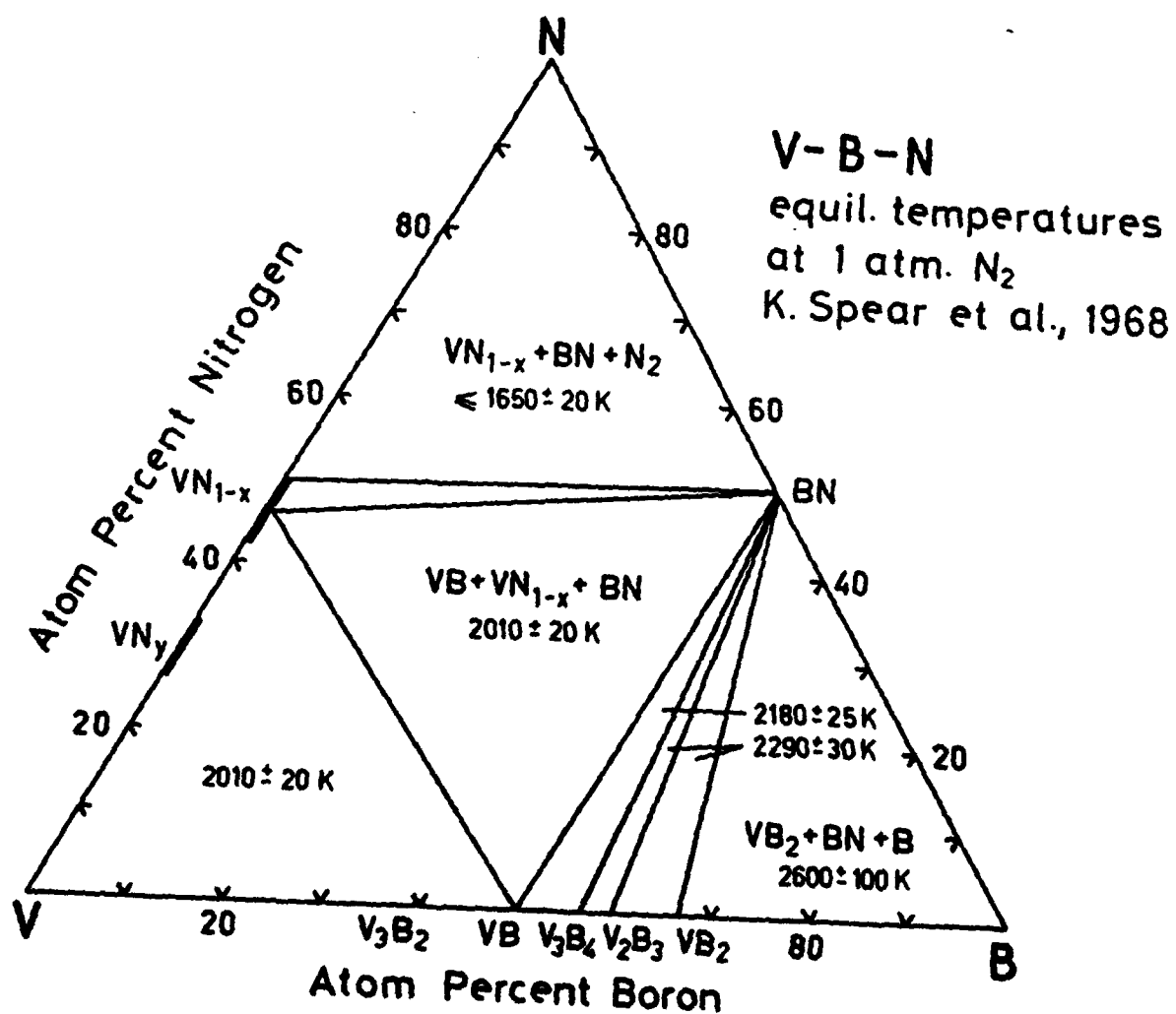




Fig.3: Isothermal section at 1200°C in the system V - B - N  
(in the absence of external nitrogen)

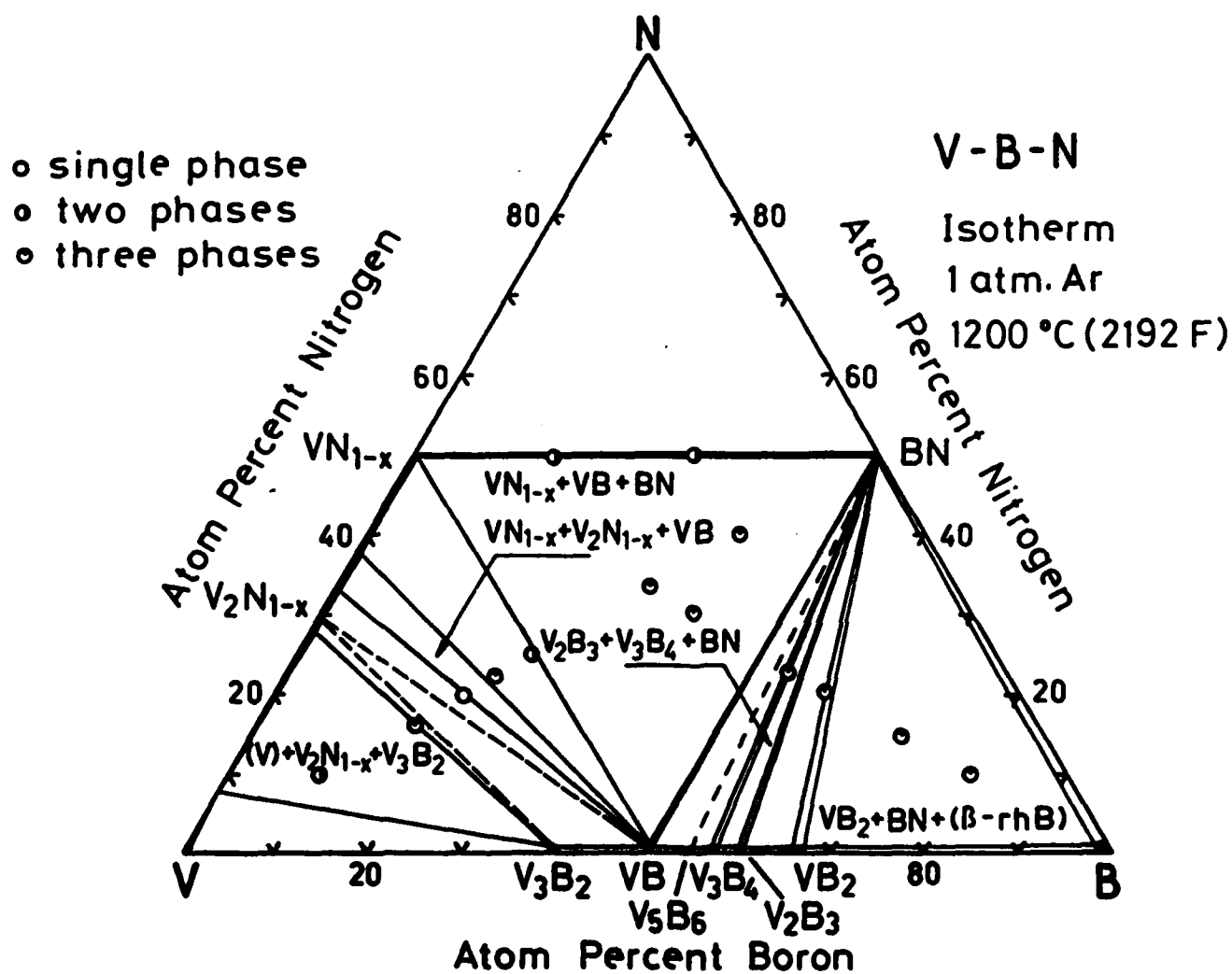
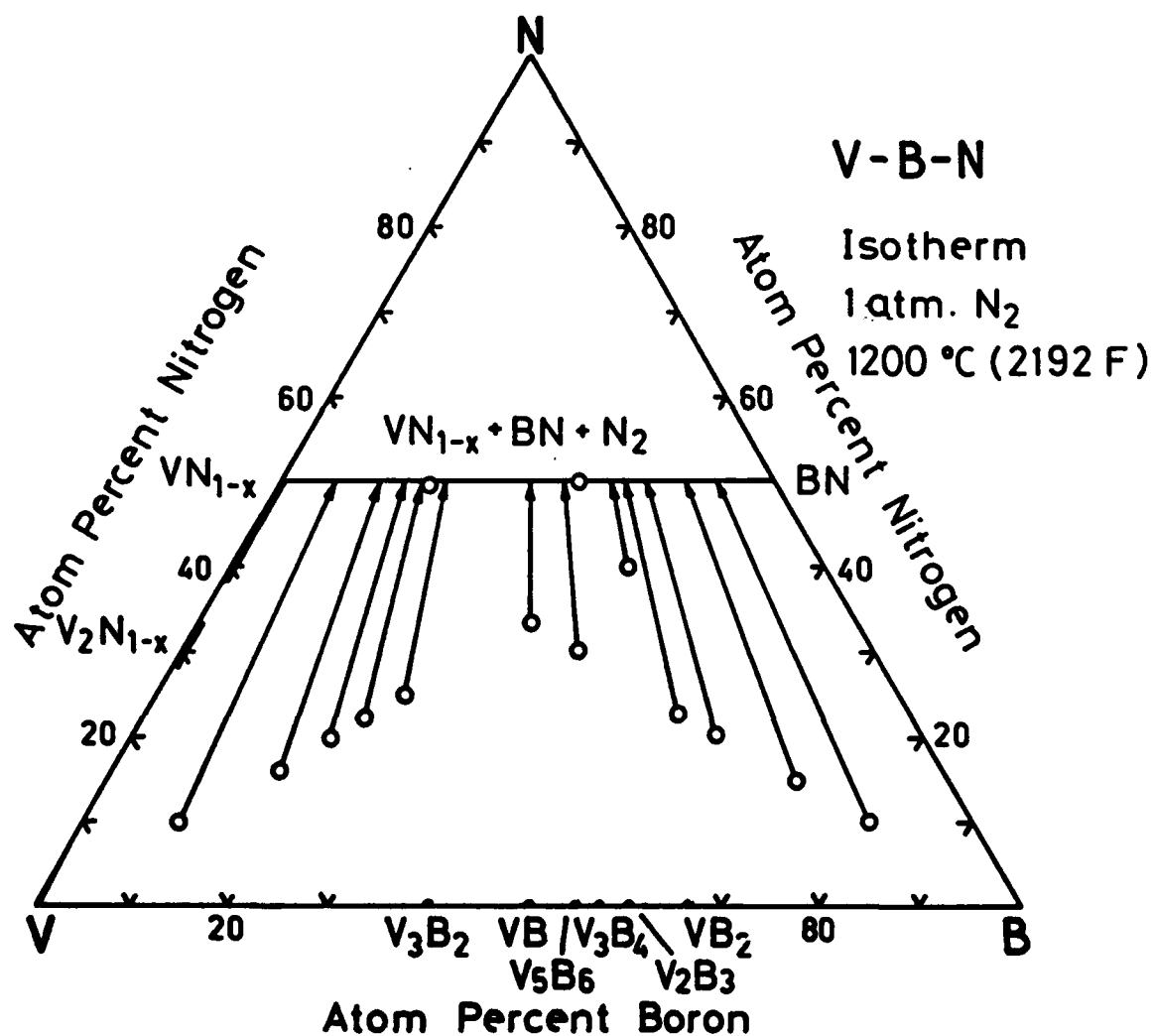


Fig.4: Isothermal section at 1200°C in the system V - B - N under 1 bar N<sub>2</sub>.



## SYSTEM BORON- NIOBIUM - NITROGEN (B-Nb-N)

### INTRODUCTION / EXPERIMENTAL

Informations on the Nb-B-N ternary are due to a recent investigation by [88Rog,89Kle] at 1400° under high vacuum or at 1200°C under 1 bar of Ar respectively. Phase relations have been established from room temperature X-ray powder diffraction analysis of about 15 binary and 30 ternary samples prepared by reaction sintering of cold compacted powder blends of B, BN, Nb, NbN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20µm in a steel mortar and/or a WC-Co mortar respectively [88Rog,89Kle]. For annealing in a 1 MHz-HF furnace ( under 1 bar of 5N-Ar or 5N-N<sub>2</sub> ) the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments usually consisted of a primary reaction at 1200°C for 70h followed by a final reaction at 1200°C up to 144h with an intermediate step of crushing and recompacting to ensure homogeneity. Treatments in vacuum (10<sup>-3</sup>Pa) usually were 64h at 1400°C. After heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Nb, crystallized boron (99.8 % B), NbN (99.8%) and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [88Rog,89Kle].

### BINARY SYSTEMS

The reinvestigation [89Kle] of the B-Nb system in the range from 900 to 1800°C revealed consistency with the data available in [84Vil], and [88Rud]; the data of [88Rud], however, are modified with respect to the formation of Nb<sub>5</sub>B<sub>6</sub> [88Rog, 89Kle]. The maximal solid solubility of boron in niobium was claimed to be less than 2 at%B at 2185°C [88Rud]; an interstitial type of B-solubility was suggested. The maximum solid solubility of Nb in β-B was reported to be less than 0.5 at% Nb at ~1800°C from X-ray powder data [81Cre] (see Table 1). Fig.1 is a representation of the constitutional diagram Nb-B.

The phase diagram for the system Nb-N is essentially based on the critical assessment by [79Pol]. A detailed discussion of solubility data, physical properties and thermodynamic data is found in [78Fro].

Crystallographic information on the binary niobium compounds is found in Table 1.

## SOLID PHASES / ISOTHERMAL SECTIONS

Figs.2,3 represent the isothermal sections at 1200°C under 1 bar Ar and at 1400°C under a vacuum of  $10^{-3}$  Pa respectively [88Rog,89Kle]. Phase equilibria are characterized by the formation of at least two ternary compounds  $Nb_2BN$  which is a superconductor ( $T_c=2.5K$ ) and a phase  $\delta$  whose crystal structure has not been solved yet. Whereas compatibility exists between the higher niobium borides and BN, niobium metal is not compatible with  $BN_{hex}$  due to the formation of a stable tie line  $NbB - Nb_2N_{1-x}$  at temperatures below 1400°C. Heating binary as well as ternary alloys at 1200°C under 1 bar  $N_2$  transfers all samples to the limiting tie line at the nitrogen rich boundary  $NbN + BN$ , equilibrium being reached after 75h of nitrogen exposure [89Kle]).

As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Nb in BN up to 1400°C, and mutual solubilities of the niobium borides, the niobium nitrides and BN up to 1200°C are rather restricted [89Kle].

## THERMODYNAMICS

A thermodynamic description of the binary system Nb-B is due to [84Kau]; see Table 2.

## REFERENCES

- [66Rud] E. Rudy and S. Windisch "The System Nb-B " Techn. Rep. AFML-TR-85-2, Part I, Vol. X, Wright Patterson Air Force Base, Oh, (1988)
- [76Pro] E. Fromm, and E. Gebhardt, "Gases and Carbon in Metals" (Springer, Berlin, 1978)
- [79Pol] C. Politis, Phase Relationships in the Nb-N and Ta-N Systems", KfK-2881 Report of Kernforschungszentrum Karlsruhe, FRG, (1979) 128-128
- [81Cre] A. J. Crespo, L. E. Tergenius and T. Lundstroem, "The Solid Solution of 4d, 5d and some p Elements in  $\beta$  Boron", J. Less-Common Met. 77 (1981) 147-150
- [84Kau] L. Kaufman, B. Uhrenius, D. Birnie and K. Taylor, "Coupled Pair Potential, Thermochemical and Phase Diagram Data for Transition Metal Binary Systems-VII", CALPHAD 8 (1984) 25-86
- [85Vil] P. Villars and L. D. Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, Oh, 1985)
- [88Rog] P. Rogl, H. Klesnar, B. Chevalier, B. Buffat, G. Denazeau and J. Etourneau, "Structural Chemistry and Phase Equilibria in the Ternary System Nb-B-N" J. Mater. Sci. Lett. 7 (1988) 1229-30
- [89Kle] H. Klesnar and P. Rogl "Phase Relations in The Ternary System : Niobium - Boron - Nitrogen", research at the Univ. Vienna, (1989) , to be published
- [90Okada] T. Okada, Private commun. (1990)
- [90Mas] T. B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., Amer. Soc. Met., Metals Park, Oh, 1990.

Table 1: Solid phases in the system B-Nb-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Nb <2489°	cI2 Im $\bar{3}$ m W	a= 330.04	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43 a=1091.91 c=2382.24	[85Vil] [85Vil] [81Cre] at 0.5at%Nb
Nb <sub>3</sub> B <sub>2</sub> <2080°	tP10 P4/mbm U <sub>3</sub> Si <sub>2</sub>	a= 619.78 c= 329.26	[89Kle]
NbB <2917°	oC8 Cmcn CrB	a= 329.74 b= 872.38 c= 316.69	[89Kle]
Nb <sub>3</sub> B <sub>6</sub>	oC22 Cmmn V <sub>3</sub> B <sub>6</sub>	a= 315.30 b=2274.4 c= 330.49	[89Kle]
Nb <sub>3</sub> B <sub>4</sub> <2935°	oI14 Immm Ta <sub>3</sub> B <sub>4</sub>	a= 330.19 b=1406.2 c= 314.51	[89Kle]
NbB <sub>2</sub> <3036°	hP3 P6/mmm AlB <sub>2</sub>	a= 311.26 c= 326.27 a= 308.61 c= 330.69	[89Kle] Nb-rich [89Kle] B- rich
Nb <sub>2</sub> N (h2)	hP9 P $\bar{3}$ 1m V <sub>2</sub> N	a= 526.7 c= 496.8	[85Vil]
$\gamma$ -Nb <sub>4</sub> N <sub>3</sub>	tI14 I4/mmm Nb <sub>4</sub> N <sub>3</sub>	a= 438.2 c= 863.2	[85Vil]

$\delta\text{-NbN}_{1-x}$	cF8 Fm3m NaCl	a= 439.4	[85Vil]
$\epsilon\text{-NbN}$	hP8 P6 <sub>3</sub> /mmc TiAs	a= 295.8 c=1127.3	[85Vil]
$\text{Nb}_5\text{N}_6$	hP22 P6 <sub>3</sub> /mmc $\text{Nb}_5\text{B}_6$	a= 519.3 c=1038.0	[85Vil]
$\text{Nb}_4\text{N}_5$	tI18 I4/m	a= 687.3 c= 429.8	[85Vil]
$\text{BN}_{\text{hex}}$	RhLi <sub>4</sub> N <sub>4</sub> hP* P6 <sub>3</sub> /mmc $\text{BN}_{\text{hex}}$	a= 250.4 c= 866.1	[85Vil]
* $\text{Nb}_2\text{BN}$	oC18 Cmcm $\text{Mo}_2\text{BC}$	a= 317.12 b=1785.04 c= 311.45	[88Rog,89Kle]
* $\text{Nb}_{85}\text{B}_{45}\text{N}_{20}$	oP*		[89Kle]

Table 2: Thermodynamic data for the system Nb-B-N

Phase	$\Delta_f G$ ( J/gramaton )	Ref.
1.0000 Nb	$\Delta_{\text{fus}} G(\text{Nb}) = 18110 - 10.275 T$	[84Kau]
1.0000 B	$\Delta_{\text{fus}} G(\text{B}) = 50210 - 21.23 T$	
1.0000 Nb	$\Delta_f G(\text{Nb}) = 0$	
0.2000 $\text{Nb}_5\text{B}_2$	$\Delta_f G(\text{Nb}_5\text{B}_2) = -51076 + 0.033 T$	
0.5000 $\text{NbB}$	$\Delta_f G(\text{NbB}) = -62722 - 0.46 T$	
0.1428 $\text{Nb}_5\text{B}_4$	$\Delta_f G(\text{Nb}_5\text{B}_4) = -70836 + 0.61 T$	
0.3333 $\text{NbB}_2$	$\Delta_f G(\text{NbB}_2) = -85548 + 2.96 T$	
1.0000 $\beta\text{B}$	$\Delta_f G(\beta\text{B}) = 0$	
Liquid(Nb,B)	$\Delta G^{\text{ex}} = x(1-x)\{-84336(1-x) - 234990x + 4.184 T\}$	
0.3333 $\text{Nb}_2\text{N}$	$\Delta_f G(\text{Nb}_2\text{N}) = -90793 + 30.96 T$	[76Fro]

Fig.1: The binary system Nb - B; based on [65Rud] and [89Kle].

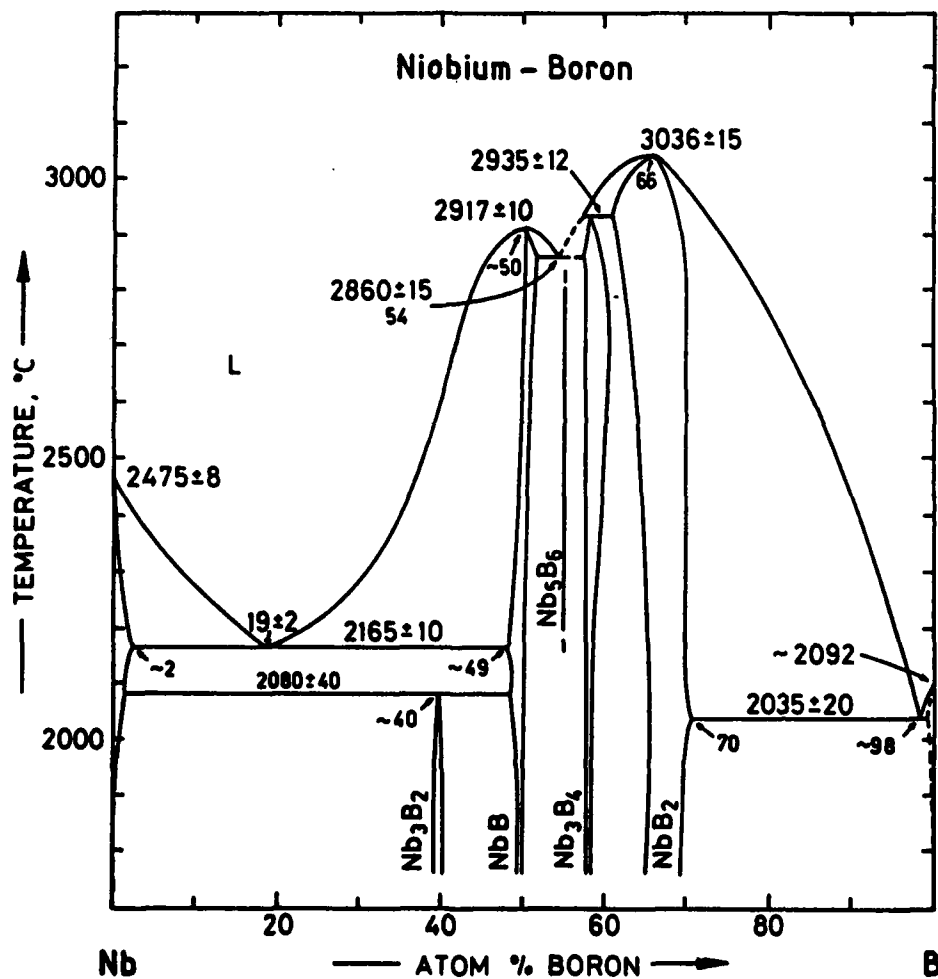




Fig.2: Isothermal section at 1200°C in the system Nb - B - N  
(in the absence of external nitrogen)

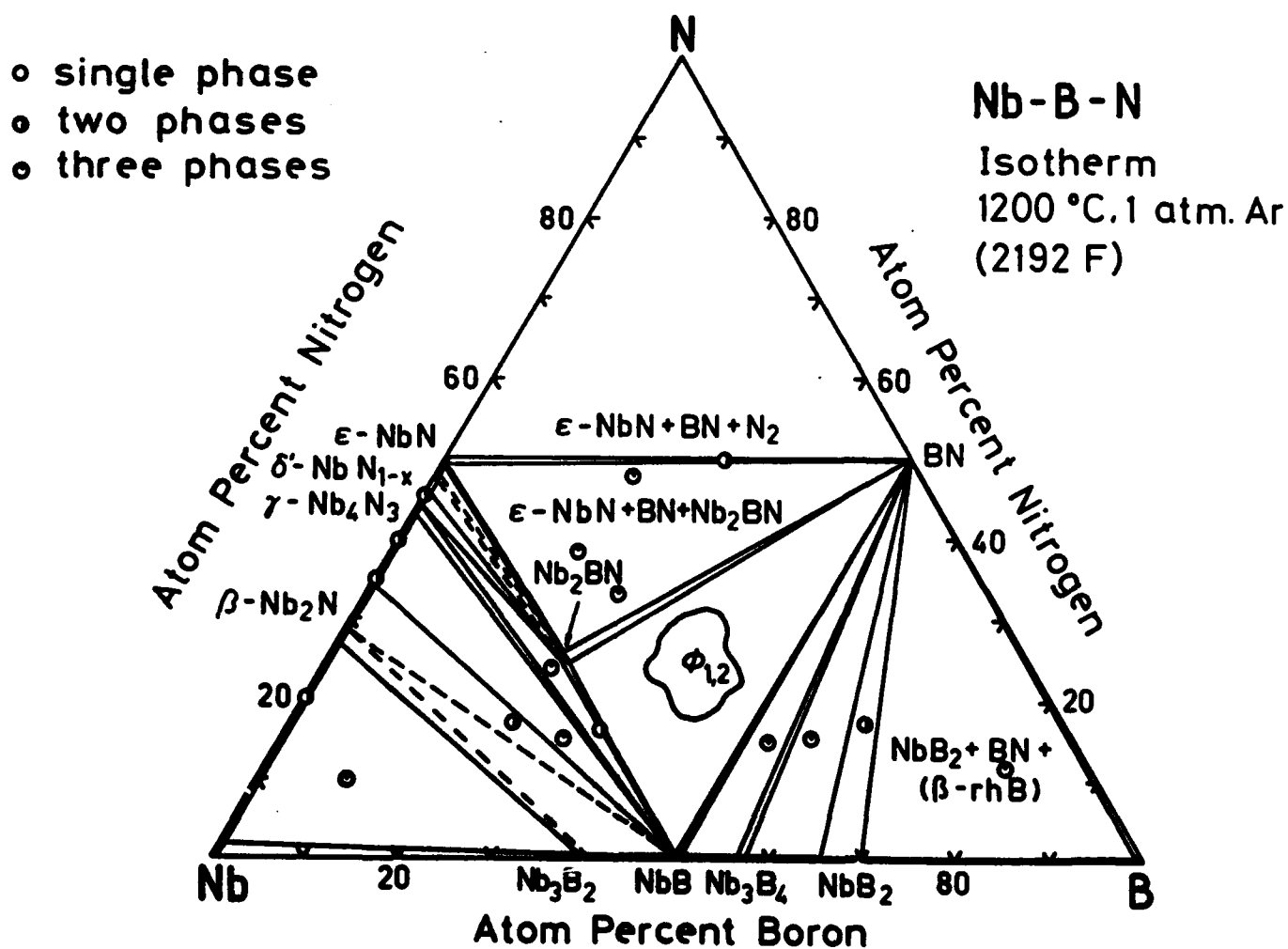
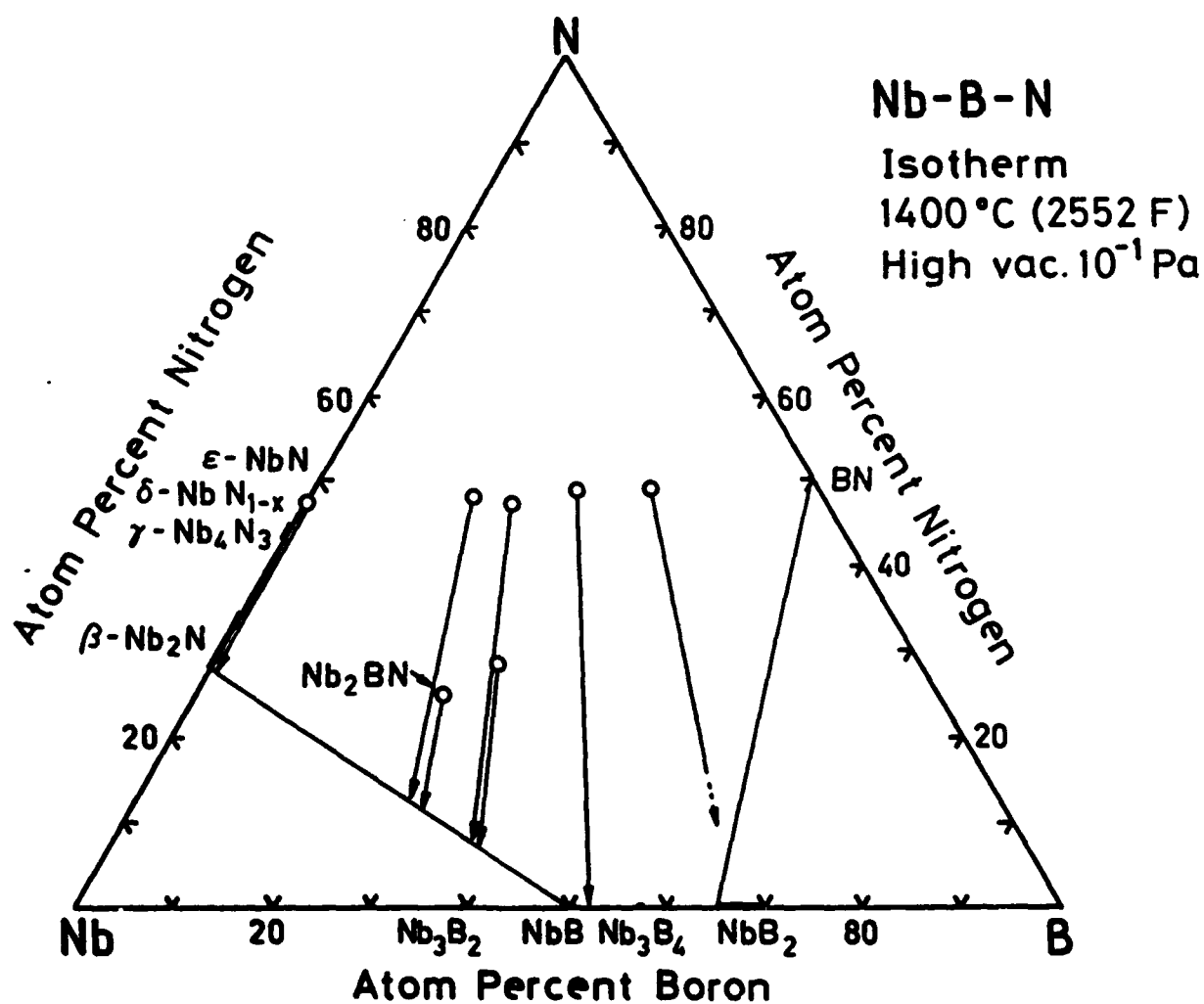


Fig.3: Isothermal section at 1400°C in the system Nb - B - N under a vacuum of  $10^{-1}$  Pa.



## SYSTEM BORON- TANTALUM - NITROGEN (B-Ta-N)

### INTRODUCTION / EXPERIMENTAL

Informations on the Ta-B-N ternary are due to a recent investigation by [89Kle] at 1400° under high vacuum or at 1200°C under 1 bar of Ar respectively. Phase relations have been established from room temperature X-ray powder diffraction analysis of about 15 binary and 25 ternary samples prepared by reaction sintering of cold compacted powder blends of B, BN, Ta, TaN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20 $\mu$ m in a steel mortar and/or a WC-Co mortar respectively [89Kle]. For annealing in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N<sub>2</sub>) the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments usually consisted of a primary reaction at 1200°C for 70h followed by a final reaction at 1200°C up to 144h with an intermediate step of crushing and recompacting to ensure homogeneity. Treatments in vacuum (10<sup>-3</sup>Pa) usually were 64h at 1400°C. After heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Ta, crystallized boron (99.8 % B), TaN (99.8%) and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [89Kle].

### BINARY SYSTEMS

The reinvestigation [89Kle] of the B-Ta system in the range from 900 to 1800°C revealed consistency with the data available in [84Vil], and [66Rud,71Por]; the data of [66Rud] are preferred, however, are modified with respect to recent reports on the existence of Ta<sub>3</sub>B<sub>8</sub> [90Ok]. The maximal solid solubility of boron in tantalum was claimed to be less than 2 at%B at 2385°C [66Rud]; an interstitial type of B-solubility was suggested. The maximum solid solubility of Ta in  $\beta$ -B was reported to be less than 0.5 at% Ta at ~1800°C from X-ray powder data [81Cre] (see Table 1). Fig.1 is a representation of the constitutional diagram Ta-B.

The phase diagram for the system Ta-N is essentially based on the work of [83Ett] and [84Koy]. A detailed discussion of solubility data, physical properties and thermodynamic data is found in [76Fro].

Crystallographic information on the binary tantalum compounds is found in Table 1.

#### SOLID PHASES / ISOTHERMAL SECTIONS

Figs. 2, 3 represent the isothermal sections at 1200°C under 1 bar Ar and at 1400°C under a vacuum of  $10^{-8}$  Pa respectively [89Kle]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between the higher tantalum borides and BN. Tantalum metal is not compatible with  $\text{BN}_{\text{hex}}$  due to the formation of a stable tie line  $\text{TaB} - \text{Ta}_2\text{N}_{1-x}$  at temperatures below 1400°C. Heating binary as well as ternary alloys at 1200°C under 1 bar  $\text{N}_2$  transfers all samples to the limiting tie line at the nitrogen rich boundary  $\text{TaN} + \text{BN}$ , equilibrium being reached after 75h of nitrogen exposure [89Kle]). High pressure experiments (1000°C, 6.0 GPa) proved the absence of hypothetical " $\text{Ta}_2\text{BN}$ " isotypic with  $\text{Nb}_2\text{BN}$  [88Rog].

As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Ta in BN up to 1400°C, and mutual solubilities of the tantalum borides, the tantalum nitrides and BN up to 1200°C are rather restricted [89Kle].

#### THERMODYNAMICS

Only limited information on the thermodynamic data of the tantalum borides and nitrides is available; see Table 2.

## REFERENCES

- [86Rud] E.Rudy and S.Windisch "The System Ta-B " Techn.Rep. AFML-TR-65-2,Part I, Vol.X, Wright Patterson Air Force Base, Oh, (1968)
- [71Por] K.I.Portnoi, V.M.Romashov and S.E.Salibekov," The System Tantalum-Boron", Poroshkov.Metall.107(11) (1971) 89-91
- [76Fro] E. Fromm, and E.Gebhardt, "Gases and Carbon in Metals" (Springer, Berlin, 1976)
- [81Cre] A.J.Crespo, L.E.Tergenius and T.Lundstroem, "The Solid Solution of 4d, 5d and some p Elements in  $\beta$  Boron", J.Less-Common Met.77 (1981) 147-150
- [83Ett] P.Ettmayer and A.Vendl," Phase Equilibria and Crystal Structures of Transition Metal Nitrides", in 'The Science of Hard Materials", R.K.Visvanadham, D.J.Rowcliffe and J.Gurland, eds. (Plenum, N.Y., 1983) 47-63
- [84Koy] T.Koyama, N.Kieda, K.Uematsu, N.Mizutani and M. Kato, "Phase Relation of Ta-N System", Yogyo Kyokai Shi 92 (1984) 255-260
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, Oh, 1985)
- [88Rog] P.Rogl, H.Klesnar, B.Chevalier, B.Buffat, G.Denazeau and J.Etourneau," Structural Chemistry and Phase Equilibria in the Ternary System Nb-B-N" J.Mater.Sci.Lett. 7 (1988) 1229-30
- [89Kle] H.Klesnar and P.Rogl "Phase Relations in The Ternary System :Tantalum - Boron - Nitrogen", research at the Univ. Vienna, (1989) ,to be published
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met., Metals Park, Oh, 1990.
- [90Oka] T.Okada, Private commun. (1990)

Table 1: Solid phases in the system B-Ta-N

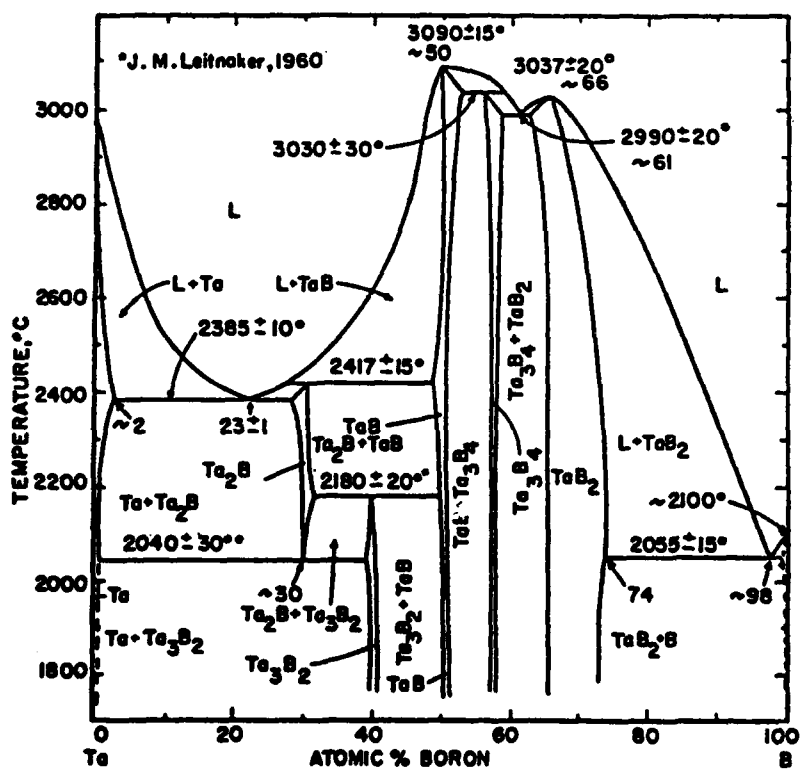
Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Ta <3020°	cI2 Im $\bar{3}$ m W	a= 330.30	[90Mas]
$\beta$ -rhB <2082°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43  a=1092.05 c=2386.73	[85Vil] [85Vil]  [81Cre] at 0.5at%Ta
Ta <sub>2</sub> B 2417-2040°	tI12 I4/mcm	a= 577.93 c= 486.38	[89Kle]
Ta <sub>3</sub> B <sub>2</sub> <2180°	tP10 P4/nbm U <sub>3</sub> Si <sub>2</sub>	a= 619.27 c= 330.27	[89Kle]
TaB <3080°	oC8 Cmcm CrB	a= 327.49 b= 868.16 c= 315.84	[89Kle]
Ta <sub>5</sub> B <sub>6</sub>	oC22 Cmmm V <sub>5</sub> B <sub>6</sub>	a= b= c=	[900ka]
Ta <sub>3</sub> B <sub>4</sub> <3030°	oI14 Immm Ta <sub>3</sub> B <sub>4</sub>	a= 328.84 b=1399.68 c= 313.20	[89Kle]
TaB <sub>2</sub> <3037°	hP3 P6/mmm AlB <sub>2</sub>	a= 309.73 c= 322.57 a= 305.86 c= 328.92	[89Kle] Ta-rich [98Kle] B- rich
Ta <sub>3</sub> N <sub>2</sub> <790°	c**	a=1010.	[85Vil]
Ta <sub>2</sub> N (h1) 2950-1650°	hP3 P6 <sub>3</sub> /mmc Fe <sub>2</sub> N	a= 304.78 c= 491.67	[85Vil]

$Ta_2N$ (h2)	hP9	a= 528.5	[85Vil]
<1850°	P $\bar{3}1m$	c= 491.9	
	$V_2N$		
$\delta-TaN_{1-x}$	cF8	a= 433.	[85Vil]
<1750°	Fm $\bar{3}m$		
	NaCl		
$\epsilon-TaN$	hP6	a= 519.6	[85Vil]
<1950°	P $\bar{6}2m$	c= 291.1	
	TaN		
$Ta_3N_5$	hP22	a= 516.	[85Vil]
	P6 $_3/nmc$	c=1027.	
	Nb $_3N_5$		
$Ta_4N_5$	tI18	a= 683.1	[85Vil]
	I4/m	c= 426.9	
	RhLi $_4N_4$		
BN <sub>hex</sub>	hP*	a= 250.4	[85Vil]
	P6 $_3/nmc$	c= 666.1	
	BN <sub>hex</sub>		

Table 2: Thermodynamic data for the system Ta-B-N

Phase	$\Delta_f G$ ( J/gramaton )	Ref.
1.0000 Ta	$\Delta_{fus} G(Ta) = 36588.2 - 11.224 T$	
1.0000 B	$\Delta_{fus} G(B) = 50210 - 21.23 T$	
1.0000 Ta	$\Delta_f G (Ta) = 0$	
1.0000 $\beta B$	$\Delta_f G (\beta B) = 0$	
0.3333 $Ta_2N$	$\Delta_f G(Ta_2N) = -87920 + 17.015 T$	[78Fro]

Fig.1: The binary system Ta - B; based on [65Rud] and [89Kle].





**Fig.2: Isothermal section at 1200°C in the system Ta - B - N  
(in the absence of external nitrogen)**

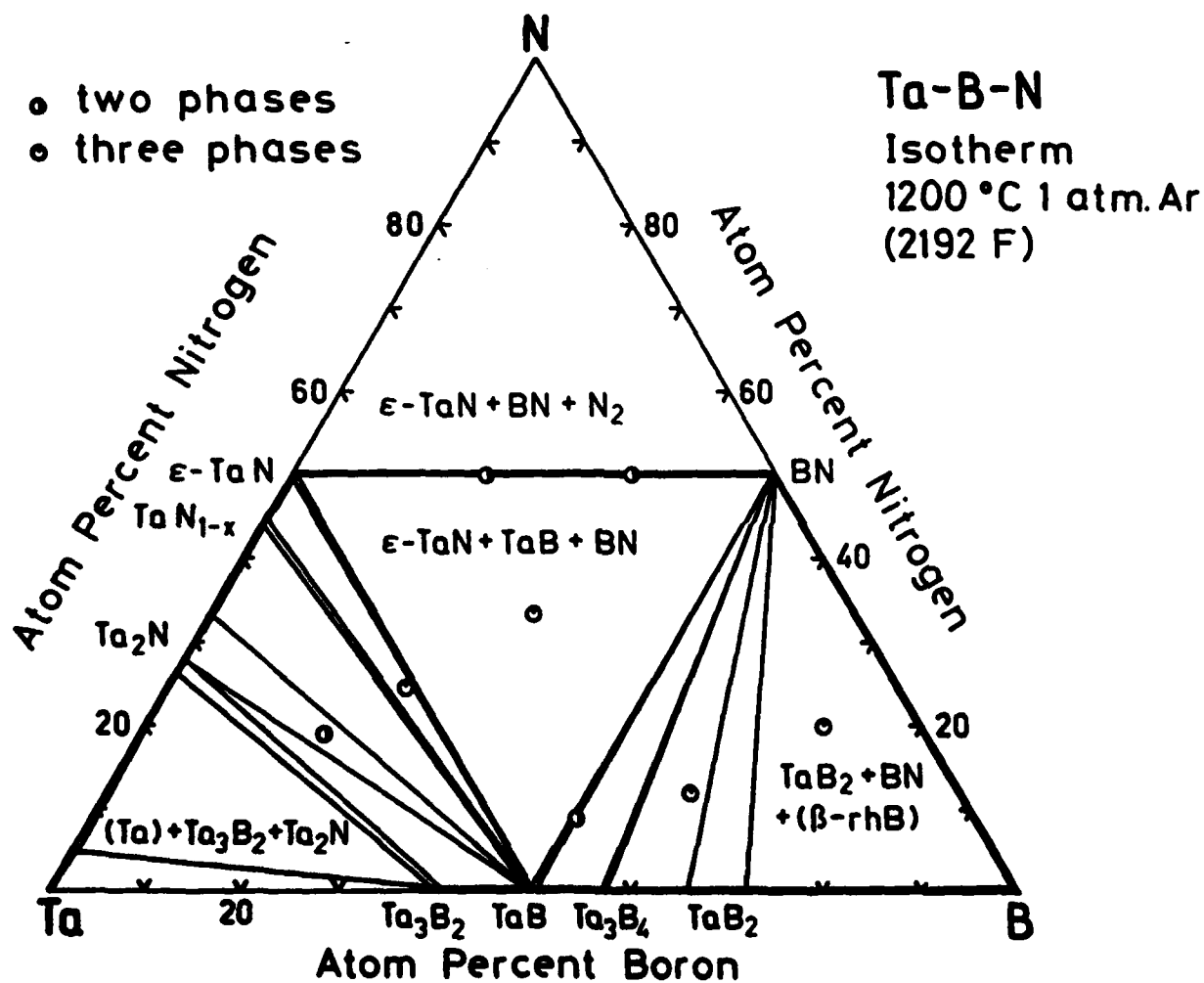
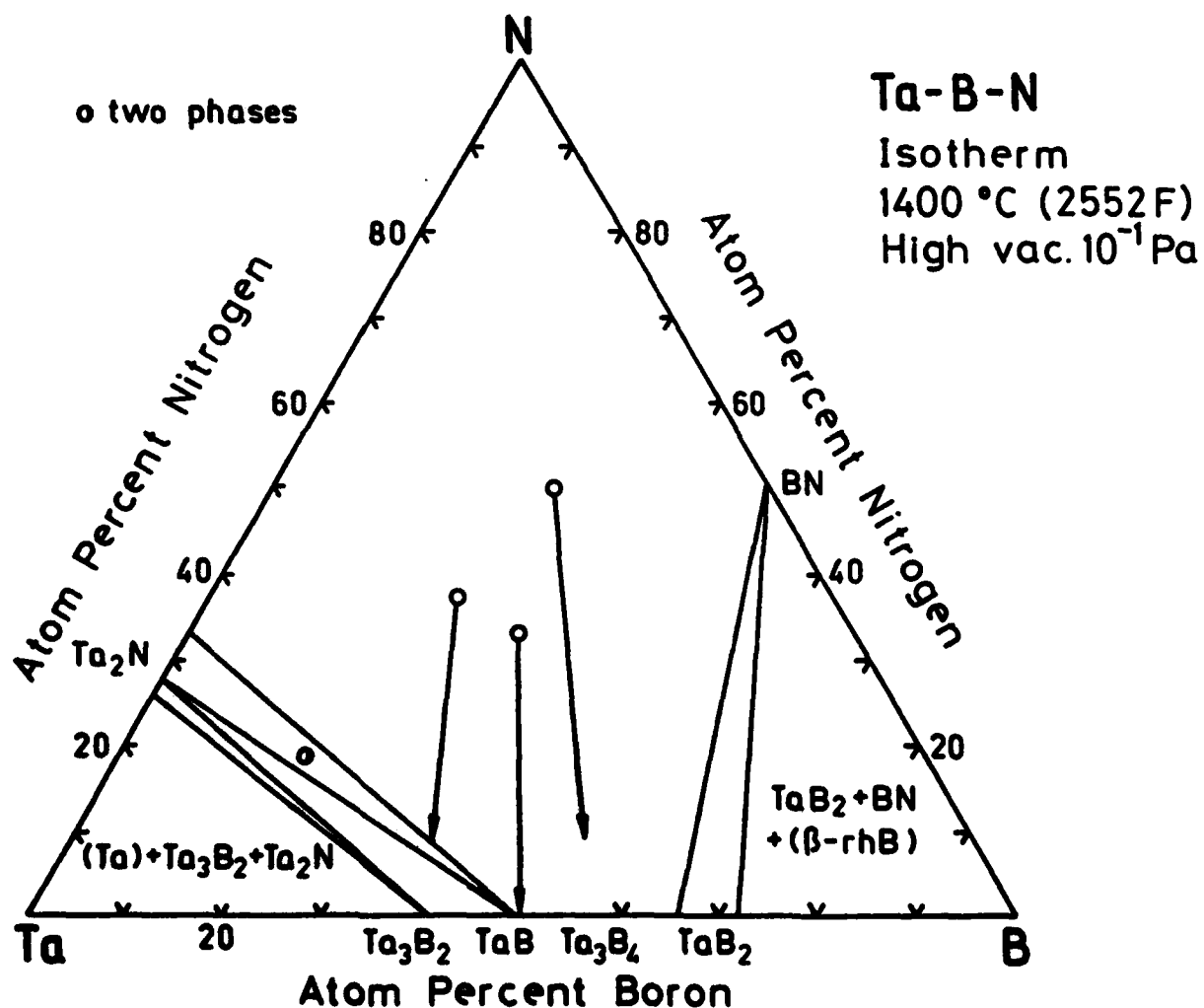


Fig.3: Isothermal section at 1400°C in the system Ta - B - N under a vacuum of  $10^{-8}$  Pa.



## SYSTEM BORON- CHROMIUM - NITROGEN (B-Cr-N)

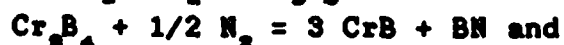
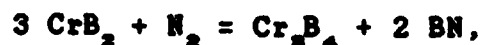
### INTRODUCTION / EXPERIMENTAL

Informations on the Cr-B-N ternary are due to [51Kis,55Bre,80Kat] and [87Šmi].

The thermal stability of binary chromium borides was investigated in a dry stream of ammonia at temperatures below 1180°C by [51Kis]. The resistance against attack by ammonia was found to increase with the boron content and no mutual solid solubilities were observed among borides and nitrides [51Kis]. Temperatures below 700°C were observed to be insufficient and chromium borides remained unchanged, whereas at temperatures 1100° and 1180°C the decomposition reaction was found to be complete for all chromium borides reaching the limiting tie line  $\text{Cr}_2\text{N} + \text{BN}$  [51Kis].

From a preliminary study of the thermodynamic stability of chromium borides [55Bre] concluded instability of the tie line  $\text{CrN} + \text{BN}$  under 0.5 bar  $\text{N}_2$  and temperatures above ca 1000°C; similarly the  $\text{Cr}_2\text{N} + \text{BN}$  equilibrium was calculated to be unstable above ca 1000 to 1200°C, and in the temperature region 1200 to 1700°C the chromium borides were said to remain stable under a partial pressure of 0.5 bar  $\text{N}_2$  [55Bre].

[80Kat] reinvestigated reactions and phase relations in the ternary system at 1600°C under 1 bar  $\text{N}_2$  revealing the formation of three-phase equilibria among two solid phases and nitrogen i.e.  $\text{Cr}_2\text{N} + \text{Cr}_2\text{B} + \text{N}$ ,  $\text{Cr}_2\text{B} + \text{Cr}_5\text{B}_3 + \text{N}$  and  $\text{Cr}_5\text{B}_3 + \text{BN} + \text{N}$ . Accordingly chromium borides with a boron content higher than  $\text{Cr}_5\text{B}_3$  were found to decompose into  $\text{Cr}_5\text{B}_3 + \text{BN}$ . For  $\text{CrB}$ , this decomposition process was demonstrated to follow a stepwise reaction path according to the following scheme being complete after 80 hrs:



Phase equilibria in the B-Cr-N system have been furthermore investigated [87Šmi] at 1000° under high vacuum or 1 bar Ar respectively and at 1400° under 1 bar Ar or 1 bar  $\text{N}_2$  respectively. Phase relations have been established from room temperature X-ray powder diffraction analysis of about 20 binary and 40 ternary samples prepared by reaction sintering of cold compacted powder blends of B,

BN, Cr,  $\text{Cr}_2\text{N}$  or CrN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than  $20\mu\text{m}$  in a steel mortar and/or a WC-Co mortar respectively [87<sup>V</sup>Sm]. For annealing in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N- $\text{N}_2$ ) the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in vacuum sealed quartz capillaries usually consisted of a primary reaction at  $1000^\circ\text{C}$  for 170h followed by a final reaction at  $1000^\circ\text{C}$  (or  $1400^\circ$  respectively) for up to 400h with an intermediate step of crushing and recompacting to ensure homogeneity. After heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Cr, crystallized boron (99.8 % B), CrN,  $\text{Cr}_2\text{N}$  (99.8%) and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at  $1400^\circ\text{C}$ . Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [87<sup>V</sup>Sm].

#### BINARY SYSTEMS

The reinvestigation [87<sup>V</sup>Sm] of the B-Cr system in the range from 900 to  $1600^\circ\text{C}$  revealed consistency with the data available in [84Vil], and [90Mas]. The maximal solid solubility of boron in chromium was claimed to be 0.72 at%B at  $1100^\circ\text{C}$  [84Sha] or 0.8 at%B at  $1500^\circ\text{C}$  [71Bor]; an interstitial type of B-solubility was suggested. The maximum solid solubility of Cr in  $\beta$ -B was reported to be less than 2.4 at% Cr at  $\sim 1800^\circ\text{C}$  from X-ray single crystal data by [70And] (see Table 1). " $\text{Cr}_2\text{B}$ ", " $\text{Cr}_3\text{B}_2$ " and tetragonal " $t\text{-Cr}_2\text{B}$ " with the  $\text{CuAl}_2$ -type were shown to be impurity phases or metastable [87<sup>V</sup>Sm]. The existence of the CrB-type has been confirmed from samples annealed above  $1000^\circ\text{C}$ , whereas alloys prepared from sinter procedures at temperatures below  $1000^\circ\text{C}$  revealed an X-ray powder pattern essentially corresponding to the MoB-type [87<sup>V</sup>Sm]. It was shown that the X-ray pattern merely arises from rather statistically than regularly occurring shifts by a vector of  $1/2(a+b)\text{CrB}$  without long range order and with an overall average length of ca  $80 \text{ \AA}$  for the undisturbed MoB-type units [87<sup>V</sup>Sm].  $\text{Cr}_3\text{B}_2$  was never observed in alloys heat treated below  $1200^\circ\text{C}$  and thus was suspected to be a high temperature compound [87<sup>V</sup>Sm]. Fig.1 is a representation of the constitutional diagram Cr-B.

The phase diagram for the system Cr-N is taken from [86Hof]

modified according to [76Fro]. The two chromium nitrides reported,  $\text{Cr}_2\text{N}$  and  $\text{CrN}$ , are unstable at  $1000^\circ\text{C}$  for  $p(\text{N}_2)$  less than 70 Pa. A detailed discussion of solubility data, physical properties and thermodynamic data is found in [76Fro].

Crystallographic information on the binary chromium compounds is found in Table 1.

#### SOLID PHASES / ISOTHERMAL SECTIONS

Figs.2-6 represent the isothermal sections at  $1600^\circ\text{C}$  under 1 bar  $\text{N}_2$  after [80Kat], and at  $1000^\circ\text{C}$  under 1 bar Ar (from alloys sealed in quartz capillaries), at  $1000^\circ\text{C}$  under high vacuum and at  $1400^\circ\text{C}$  under 1 bar Ar (in the absence of external nitrogen pressure) and under 1 bar  $\text{N}_2$  respectively [87<sup>V</sup>Sm]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between the higher chromium borides and BN. Chromium metal is not compatible with  $\text{BN}_{\text{hex}}$  due to the formation of a stable tie line  $\text{Cr}_2\text{B} - \text{Cr}_2\text{N}$  at  $1000^\circ\text{C}$ . The limiting tie line  $\text{CrN} + \text{BN}$  and the formation of a three-phase equilibrium  $\text{CrN} + \text{BN} + \text{N}$  at  $1000^\circ\text{C}$  is due to nitrogen build-up within the sealed quartz capsules stabilizing  $\text{CrN}$  (Fig.3). Application of a high vacuum ( $10^{-4}\text{Pa}$ ) at  $1000^\circ\text{C}$  results in a rapid decomposition of  $\text{CrN} + \text{BN}$  into  $\text{Cr}_2\text{N} + \text{BN}$  followed by a subsequent but rather slow decomposition of  $\text{Cr}_2\text{N}$  (Fig.4, [87<sup>V</sup>Sm]) in perfect agreement with the decomposition pressure of the binary chromium nitrides (see [76Fro, 70Mil]).

Phase equilibria at  $1400^\circ\text{C}$  and 1 bar Ar are characterized by the instability of  $\text{CrN}$  and  $\text{Cr}_2\text{N}$  and by an increased stability of the binary chromium borides against nitrogen (Fig.5). Heating binary as well as ternary alloys at  $1400^\circ\text{C}$  under 1 bar  $\text{N}_2$  transfers all samples to the limiting tie line at the nitrogen rich boundary  $\text{Cr}_2\text{N} + \text{BN}$ , equilibrium being reached after 75h of nitrogen exposure (Fig.6, [87<sup>V</sup>Sm]).

As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Cr in BN up to  $1600^\circ\text{C}$ , and mutual solubilities of the chromium borides, the chromium nitrides and BN up to  $1600^\circ\text{C}$  are rather restricted [80Kat, 87<sup>V</sup>Sm].

## THERMODYNAMICS

A thermodynamic modelling of the binary system Cr-B is due to [86Lia]; see Table 2. Thermodynamic data of the chromium nitrides are due to [76Pro] and [70Mil].

## REFERENCES

- [51Kis] R.Kiessling and Y.H.Liu, "Thermal Stability of the Chromium, Iron, and Tungsten Borides in Streaming Ammonia and the Existence of New Tungsten Nitride", Trans. AIME - J.Metals 3 (1951) 639
- [64Sha] F.I.Shamrai and T.F.Fedorov in "Issledovaniya Metallov. v. Zhidkom. Tverdom Sostoyaniyakh", (Izd. Nauka, Moscow, 1964) 255-264
- [70Mil] T.Mills, "Thermodynamic Relations in the Chromium-Nitrogen System", J.Less-Common Met. 22 (1970) 373-81
- [70And] S.Andersson and T.Lundstroem, "The Solubility of Cr in  $\beta$ -Rh Boron as determined in  $\text{CrB}_{41}$  by Single Crystal Diffractometry", J.Solid State Chem. 2 (1970) 603-611
- [71Bor] M.L.Borlera and G.Pradelli, "The System Chromium Boron", La Metallurgia Italiana 63 (1971) 61
- [76Pro] E. Fromm and E.Gebhardt, "Gases and Carbon in Metals" (Springer, Berlin, 1976)
- [80Kat] T.Kato, S.Hirano, M.Yoshimura and S.Soeniya, "Reactions and Phase Relations in The System Cr-B-N under 1 Atm  $\text{N}_2$ ", Yogyo-Kyokai-Shi 88 (1980) 345-352
- [81Cre] A.J.Crespo, L.E.Tergenius and T.Lundstroem, "The Solis Solution of 4d, 5d and some p Elements in  $\beta$ - Rhombohedral Boron", J. Less-Common Metals, 77 (1981) 147-150
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Aner.Soc.Met., Metals Park, Oh, 1985)
- [86Lia] P.K.Liao and K.E.Spear, "The B-Cr System", Bull.Alloy Phase Diagrams 7 (1986) 232-237
- [87Oka] S.Okada, T.Atoda and I.Higashi, "Structural Investigation of  $\text{Cr}_2\text{B}_3$ ,  $\text{Cr}_3\text{B}_4$  and CrB by Single Crystal Diffractometry"

J.Solid State Chem. 88 (1987) 61-67

[87Šmi] I.Šmid and P.Rogl "Phase Relations in The Ternary System :Chromium - Boron - Nitrogen", research at the Univ. Vienna, (1987) ,to be published

[90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., Amer.Soc.Met., Metals Park,Oh, 1990.

Table 1: Solid phases in the system B-Cr-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Cr <1863°	cI2 Im $\bar{3}$ m W	a= 388.48	[90Mas]
$\beta$ -rhB <2082°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43 a=1096.66 c=2385.14	[85Vil] [85Vil] [81Cre] at 2.4at%Cr
Cr <sub>2</sub> B <1870°	oF40 Fddd o-Mn <sub>2</sub> B	a=1470.6 b= 741.33 c= 425.35	[87Šmi]
Cr <sub>3</sub> B <sub>2</sub> <1900°C	tI32 I4/mcm Cr <sub>3</sub> B <sub>2</sub>	a= 546.40 c=1011.0	[87Šmi]
T-CrB <1000°	tI18 Transpos.Type $\alpha$ -MoB-rel.	a=294.93 b= 786.4 c= 294.32	[87Šmi]
$\beta$ -CrB <2085°	oC8 Cmcm CrB	a= 296.89 b= 786.89 c= 293.33	[87Šmi]
Cr <sub>3</sub> B <sub>4</sub> <2075°	oI14 Immm Ta <sub>3</sub> B <sub>4</sub>	a= 298.56 b=1302.2 c= 295.25	[87Šmi]

$\text{Cr}_2\text{B}_9$	$\text{oC20}$	$a = 302.84$	[870ka]
	$\text{Cmcm}$	$b = 1811.5$	
	$\text{V}_2\text{B}_9$		
$\text{CrB}_2$ <2200°	$\text{hP3}$	$a = 297.32$	[87 <sup>V</sup> mi]
	$\text{P6}/\text{mmm}$	$c = 307.25$	
	$\text{AlB}_2$		
$\text{CrB}_4$ <1450°	$\text{oI10}$	$a = 474.99$	[87 <sup>V</sup> mi]
	$\text{Immm}$	$b = 547.89$	
	$\text{CrB}_4$	$c = 286.82$	
$\text{Cr}_2\text{N}$	$\text{hP9}$	$a = 479.6$	[85Vil]
	$\text{P6}_322$	$c = 447.0$	
	$\text{Mn}_2\text{N}_{0.88}$		
$\text{CrN}$	$\text{cF8}$	$a = 414.8$	[87 <sup>V</sup> mi]
	$\text{Fm}\bar{3}\text{m}$		
	$\text{NaCl}$		
$\text{BN}_{\text{hex}}$	$\text{hP*}$	$a = 250.4$	[85Vil]
	$\text{P6}_3/\text{mmc}$	$c = 666.1$	
	$\text{BN}_{\text{hex}}$		

Table 2: Thermodynamic data for the system Cr-B-N

Phase	$\Delta_f G$ ( J/gramatom )	Ref.
1.0000 Cr	$\Delta_{\text{fus}} G(\text{Cr}) = 21004 - 9.6349 T$	[86Lia]
1.0000 B	$\Delta_{\text{fus}} G(\text{B}) = 50210 - 21.23 T$	
1.0000 Cr	$\Delta_f G(\text{Cr}) = 0$	
0.3333 $\text{Cr}_2\text{B}$	$\Delta_f G(\text{Cr}_2\text{B}) = -28285 - 0.330 T$	[76Fro]
0.1250 $\text{Cr}_5\text{B}_9$	$\Delta_f G(\text{Cr}_5\text{B}_9) = -36700 - 2.300 T$	
0.5000 $\text{CrB}$	$\Delta_f G(\text{CrB}) = -39920 + 0.395 T$	
0.1429 $\text{Cr}_9\text{B}_4$	$\Delta_f G(\text{Cr}_9\text{B}_4) = -40788 - 0.584 T$	
0.3333 $\text{CrB}_2$	$\Delta_f G(\text{CrB}_2) = -41432 + 0.818 T$	
0.2000 $\text{CrB}_4$	$\Delta_f G(\text{CrB}_4) = -24723 + 0.400 T$	
1.0000 $\beta\text{B}$	$\Delta_f G(\beta\text{B}) = 0$	
Liquid(Cr,B)	$\Delta G^{\text{ex}} = x(1-x)\{-181050 + 35.66 T + 52800(1-2x) + 18600(1-2x)^2 - 34200(1-2x)^3 + 13700(1-2x)^4\}$	
0.3632 $\text{Cr}_2\text{N}_{0.76}$	$\Delta_f G = -30883.4 + 15.22 T$	



**Fig.1: The binary system Cr - B; based on [71Pra,86Mas] and [87Šni].**

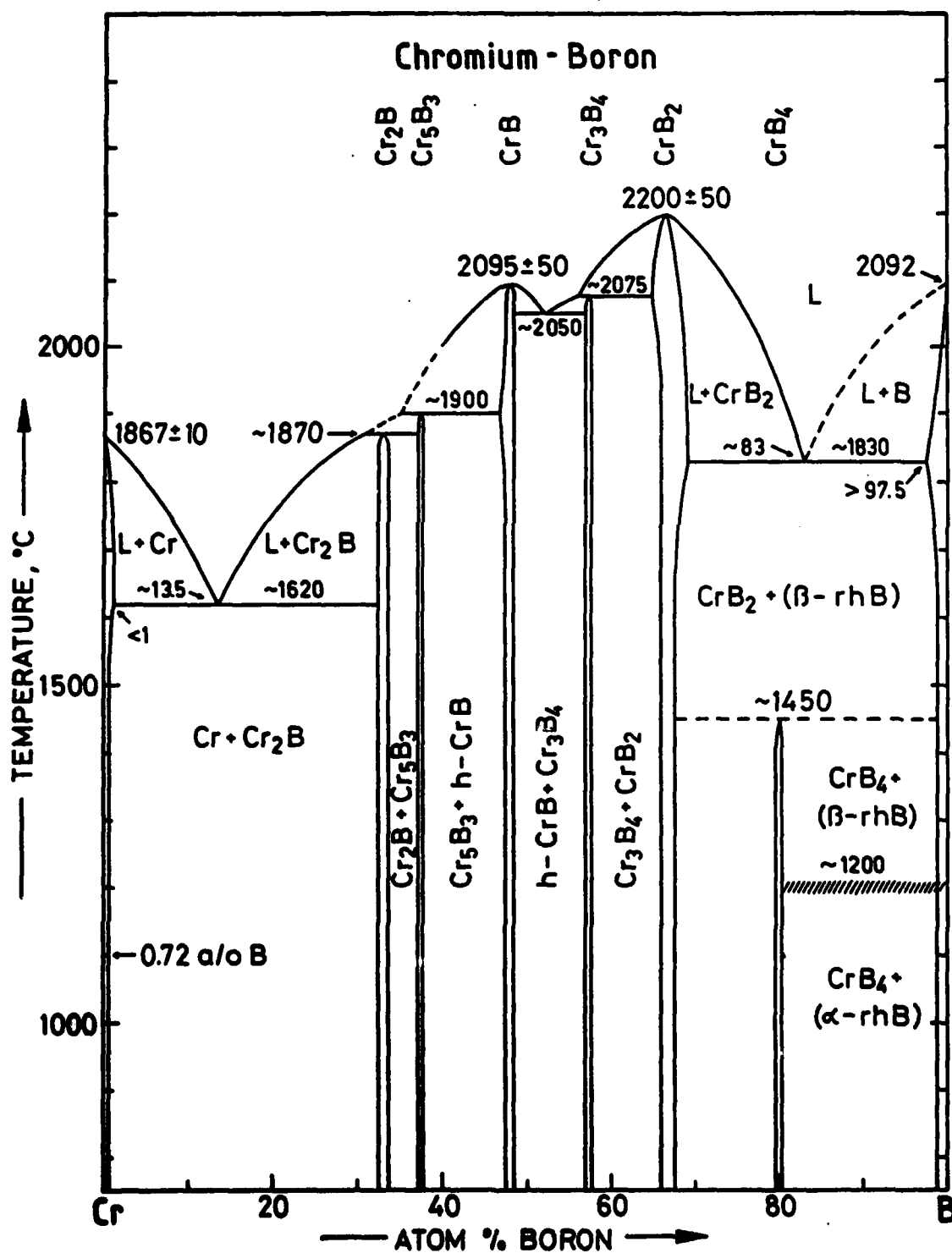


Fig.2: Isothermal section at 1600°C in the system Cr - B - N  
under 1 bar N<sub>2</sub> ( after [80Kat] )

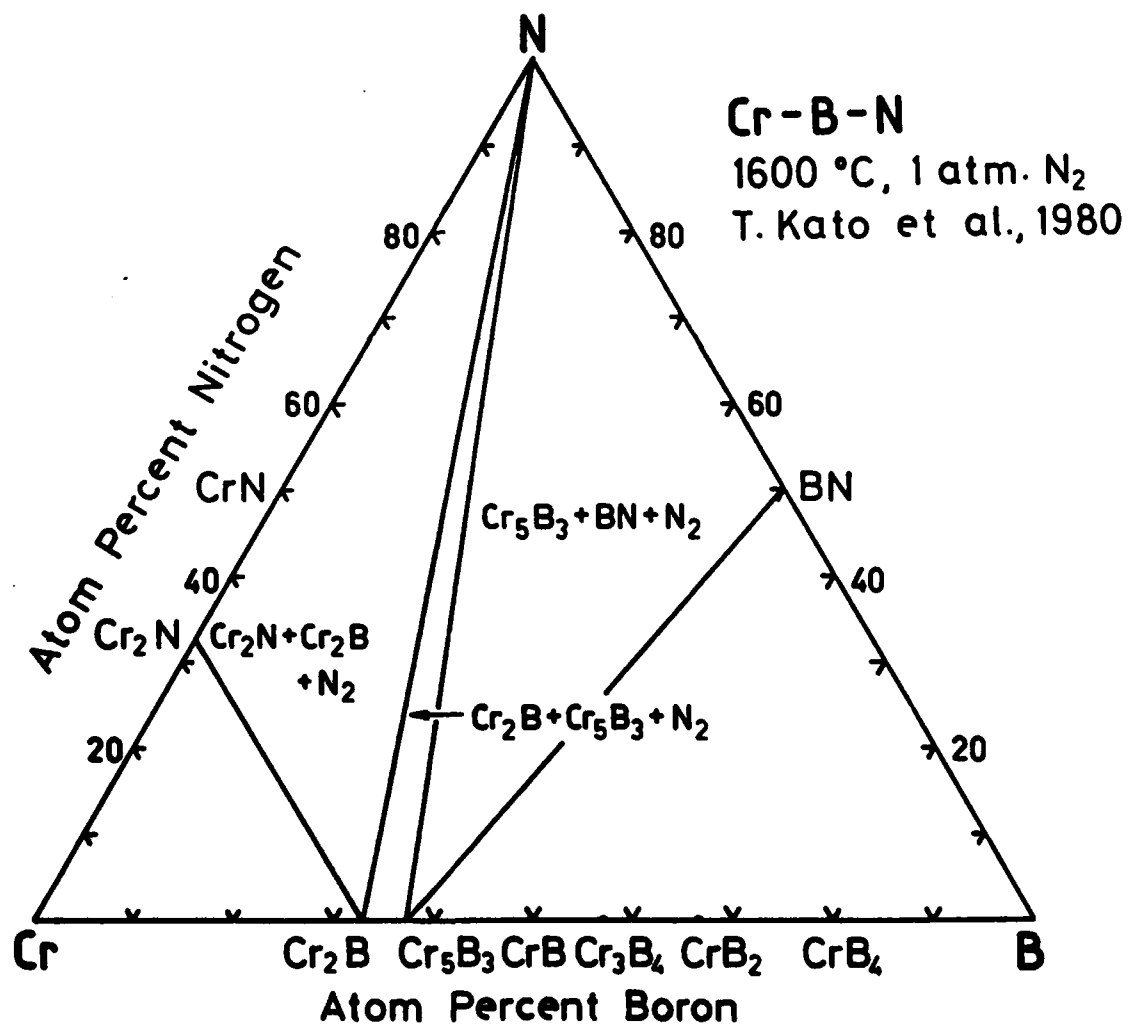


Fig.3: Isothermal section at 1000°C in the system Cr - B - N  
from samples sealed in quartz capillaries (in the absence of  
external nitrogen)

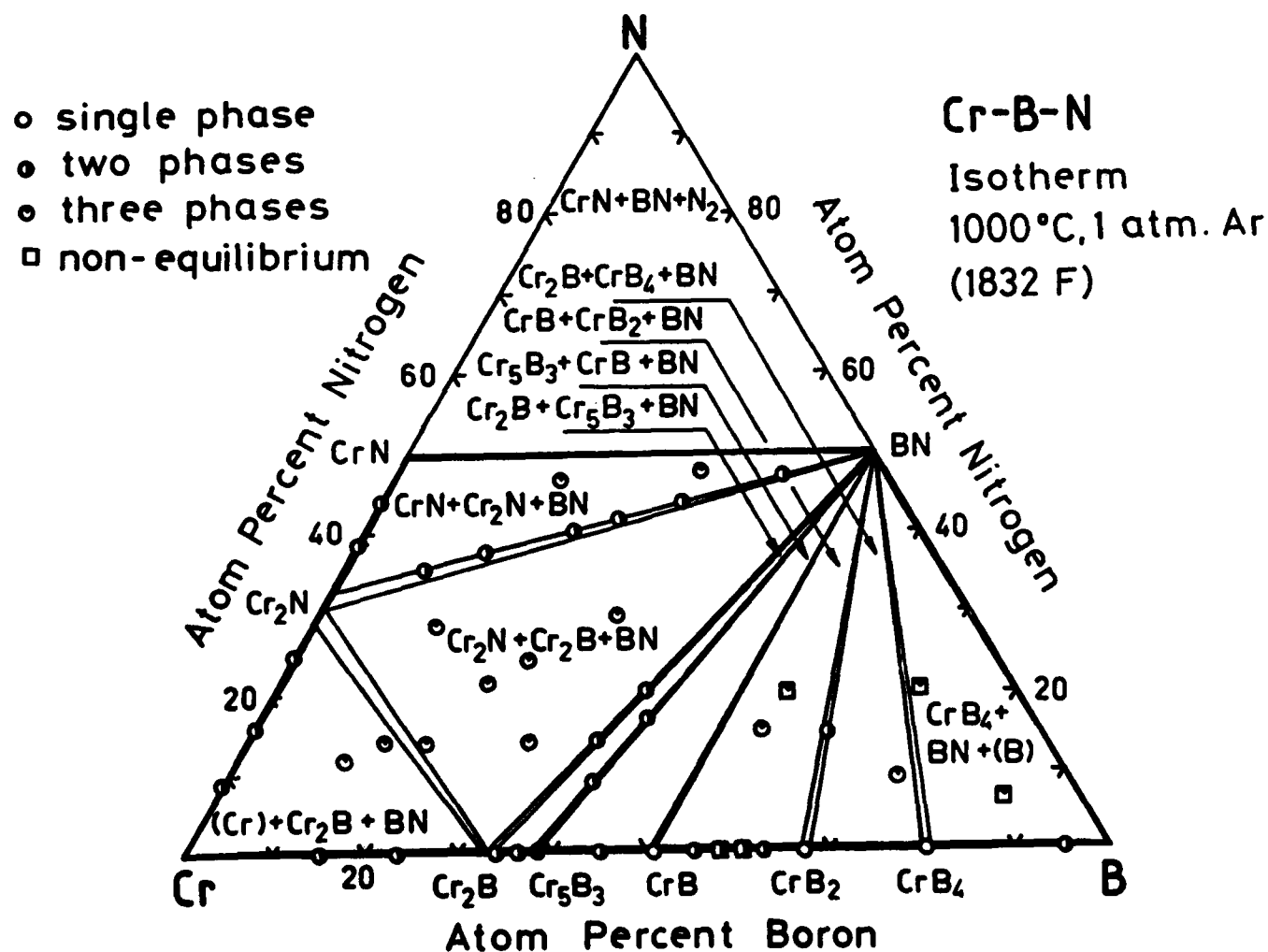


Fig.4: Isothermal section at 1000°C in the system Cr - B - N  
under a high vacuum ( $10^{-6}$  Pa)

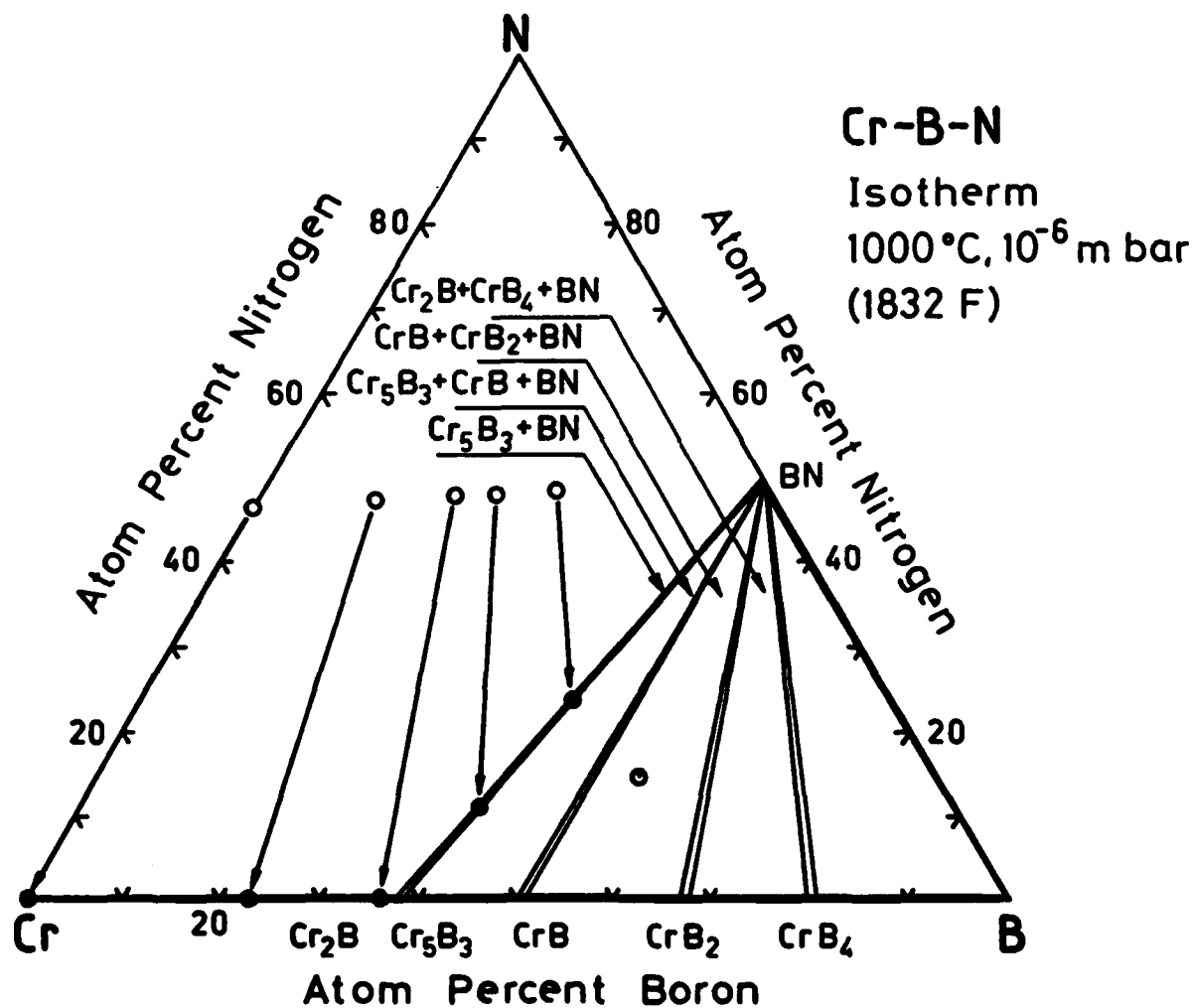


Fig.5: Isothermal section at 1400°C in the system Cr - B - N  
under 1 bar Ar ( in the absence of external nitrogen  
pressure)

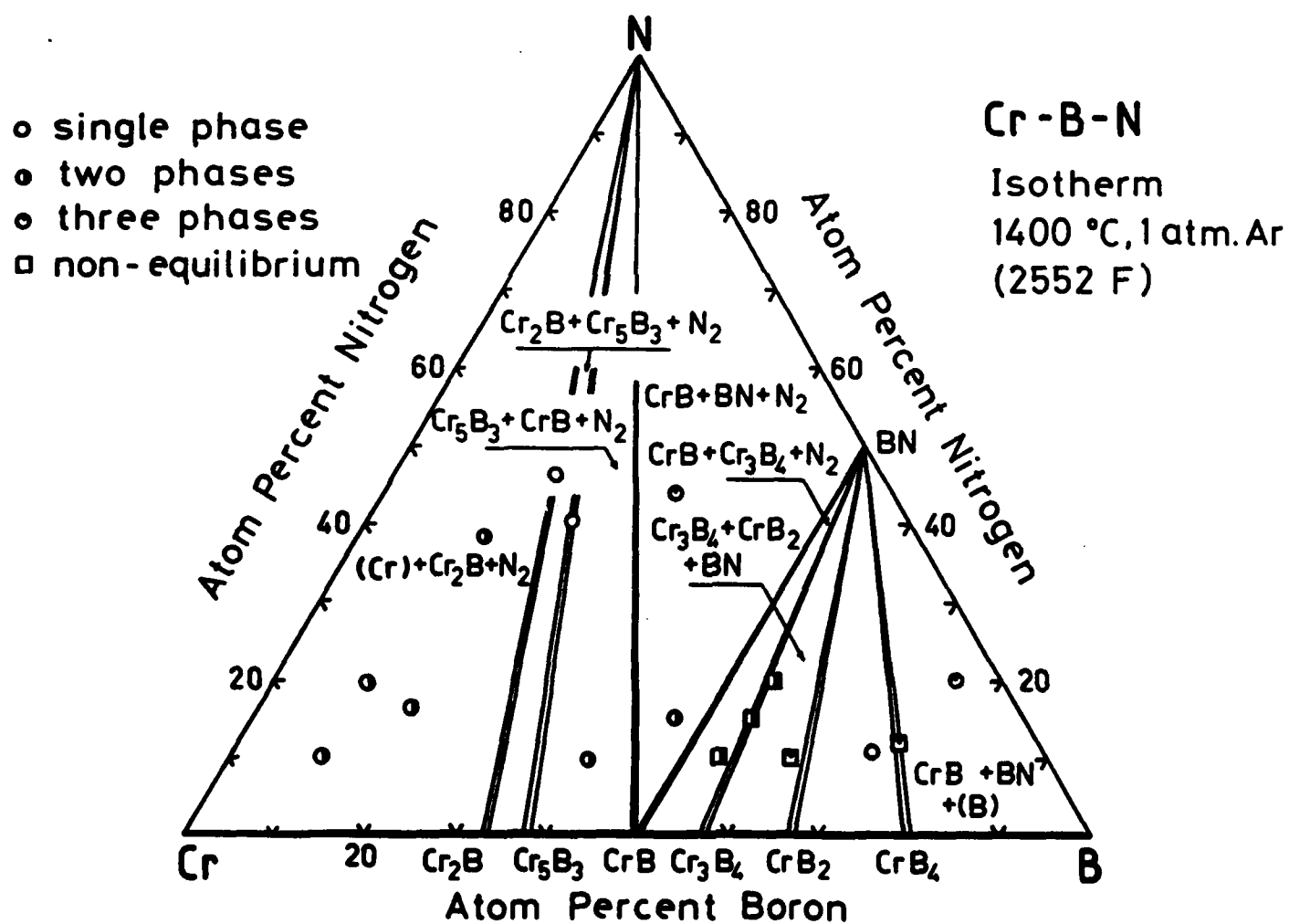
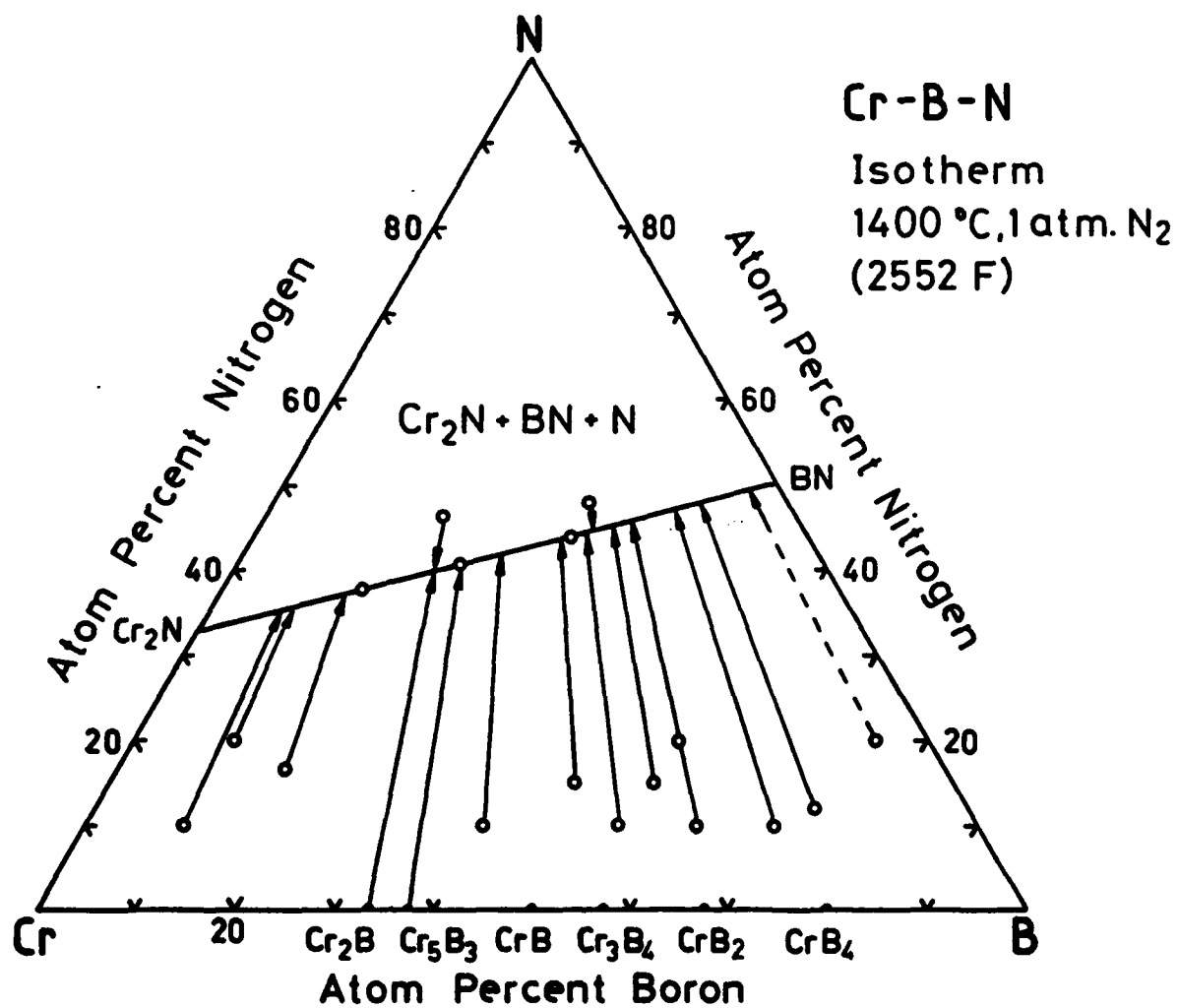


Fig.6: Isothermal section at 1400°C in the system Cr - B - N under 1 bar N<sub>2</sub>



## SYSTEM BORON- MOLYBDENUM - NITROGEN (B-Mo-N)

### INTRODUCTION / EXPERIMENTAL

Informations on the Mo-B-N ternary are due to [89Bae1,2] (see section *Thermodynamics*) and [88Kle].

Phase equilibria in the B-Mo-N system have been established at 1200°, 1400°, and 1600°C from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, Mo, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20  $\mu$ m in a steel mortar and/or a WC-Co mortar respectively [88Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N<sub>2</sub>) usually consisted of a primary reaction at 1200°C for 36h followed by a final reaction at 1200°C or 1400°, 1600°C respectively for up to 64h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Mo, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [88Kle].

### BINARY SYSTEMS

The reinvestigation of the B-Mo system in the range from 1200 to 1600°C revealed consistency with the data available in [84Vil], and [90Mas] amended by mass spectrometer data of [77Sto] determining the homogeneous ranges of the molybdenum borides. The solid solubility of boron in molybdenum was claimed to be less than 2 at%B at the Mo-Mo<sub>2</sub>B eutectic temperature (2175°C); an interstitial type of B-solubility was suggested [65Rud]. The maximum solid solubility of Mo in  $\beta$ -B was reported to be less than 0.5 at% Mo at ~1800°C [65Rud] in agreement with X-ray data by [81Cre] (see Table 1). Fig.1 is a representation of the constitutional diagram Mo-B.

The phase diagram for the system Mo-N in [90Mas] is based on the

original diagrams of [70Ett] and [78Jeh]; a critical assessment including the region below 1000°C is due to [80Bre]. The binary molybdenum nitrides are unstable at  $T > 1000^{\circ}\text{C}$  and  $p(\text{N}_2) < 10^5 \text{ Pa}$  [78Jeh]. A detailed discussion of solubility data, physical properties and thermodynamic data is found in [78Fro].

## SOLID PHASES / ISOTHERMAL SECTIONS

Figs.2-4 represent the isothermal sections at 1200°C, 1400°C and 1600°C under 1 bar of argon (in the absence of external nitrogen pressure) [88Kle]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between the higher molybdenum borides and BN. Phase equilibria were found to be rather dependent on the nitrogen partial pressure. The stability of the (Mo + BN)- and the (Mo<sub>2</sub>B+BN)-two phase equilibria as a function of  $T$  and  $p(\text{N}_2)$  were investigated [88Kle] in good agreement to earlier data by [89Bae1,2] and confirm the observed phase equilibria ( see also section *Thermodynamics* ). Thus at 1200°C and under 1 bar Ar (Mo + BN) decomposes to Mo<sub>2</sub>B + N<sub>2</sub>, and similarly at higher temperatures (1400, 1600°C) the subboride Mo<sub>2</sub>B becomes incompatible with BN and decomposes under formation of MoB + N<sub>2</sub> [88Kle]. Phase equilibria were furthermore checked at 1400°C applying a vacuum of 10<sup>-4</sup>Pa for 100h revealing a rapid decomposition of (Mo+BN) starting compositions into Mo<sub>2</sub>B, MoB, and MoB+BN [88Kle]. The kinetic of nitriding binary molybdenum borides was studied at 1200 and 1400°C under 1 bar of 6N-N<sub>2</sub> and confirmed the phase equilibria in Figs.2-4 [88Kle].

As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Mo in BN up to 1000°C, and mutual solubilities of the molybdenum borides and BN up to 1600°C are rather restricted [88Kle].

## THERMODYNAMICS

A thermodynamic modelling of the binary system Mo-B is due to [88Spe]; see Table 2.



[69Bae1,2] studied the reaction of Mo and BN using a Thermobalance. From these measurements the activation energies for the formation of the binary borides were derived. Furthermore the onset of the reaction  $2\text{Mo} + \text{BN} \rightleftharpoons \text{Mo}_2\text{B} + 1/2\text{N}_2$  was measured as a function of the nitrogen partial pressure yielding free enthalpy data for the reaction and data for the free enthalpy of formation for  $\text{Mo}_2\text{B}$ .

## REFERENCES

- [65Rud] E. Rudy and S. Windisch, " The System Molybdenum - Boron ", AFML-Technical Report 2, Part I, Vol. III, Wright Patterson Air Force Base, Ohio (1965) pp. 1-72
- [69Bae1] F.D. Baehren and D. Vollath, " A Determination of The Thermodynamic Data of The Borides  $\text{Mo}_2\text{B}$ ,  $\text{W}_2\text{B}$  and  $\text{Re}_2\text{B}$ " (in German), *Planseeber.f. Pulvermetall.*, 17 (1969) 180-183
- [69Bae2] F.D. Baehren, F. Thuemmler and D. Vollath, "The Kinetic of The Formation of The Borides of Molybdenum, Tungsten and Rhenium from Boron Nitride-Metal Powder Mixtures" (in German), *J. Less-Common Metals*, 18 (1969) 295-303
- [70Ett] P. Ettmayer, "The System Molybdenum - Nitrogen", *Monatsh. Chemie* 101 (1970) 127-140
- [76Fro] E. Fromm, and E. Gebhardt, "Gases and Carbon in Metals" (Springer, Berlin, 1976)
- [78Jeh] H. Jehn and P. Ettmayer, "The Molybdenum - Nitrogen Phase Diagram", *J. Less-Common Met.* 58 (1978) 85-98
- [80Bre] L. Brewer and J. Lamoreaux, " The Mo-N (Molybdenum-Nitrogen) System", *Bull. Alloy Phase Diagrams* 1 (1980) 82-85
- [81Cre] A.J. Crespo, L.E. Tergehius and T. Lundstroem, *J. Less-Common Metals*, 77 (1981) 147
- [85Vil] P. Villars and L.D. Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, Oh, 1985)
- [88Kle] H. Klesnar and P. Rogl "Phase Relations in The Ternary System :Molybdenum - Boron - Nitrogen", research at the Univ. Vienna, (1988) ,to be published
- [88Spe] K.E. Spear and P.K. Liao, "The B-Mo System", *Bull. Alloy Phase Diagrams* 9 (1988) 457-466
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams" ,2<sup>nd</sup> Ed., Amer. Soc. Met., Metals Park, Oh, 1990.

Table 1: Solid phases in the system B-Mo-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Mo <2623°	cI2 Im $\bar{3}$ m W	a= 314.70	[80Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43 a=1093.03 c=2382.17	[85Vil] [85Vil] [81Cre] at 0.5at%Mo
Mo <sub>2</sub> B <2280°	tI12 I4/mcm Al <sub>2</sub> Cu	a= 554.80 c= 474.06	[88Kle]
$\alpha$ -MoB <2180°	tI16 I4 <sub>1</sub> /and $\alpha$ -MoB	a= 310.88 c=1696.18	[88Kle]
$\beta$ -MoB <2600°	oC8 Cmcm CrB	a= 314.02 b= 848.90 c= 307.10	[88Kle]
MoB <sub>2</sub> 2375-1517°	hP3 P6/mmm AlB <sub>2</sub>	a= 303.78 c= 306.03	[88Kle]
Mo <sub>2</sub> B <sub>3</sub> <2140°	hR7 R $\bar{3}$ m Mo <sub>2</sub> B <sub>3</sub>	a= 301.17 c=2094.9	[88Kle]
Mo <sub>1-x</sub> B <sub>3</sub> <1807°	hP P6 <sub>3</sub> /mmc W <sub>1-x</sub> B <sub>3</sub>	a= 520.36 c= 635.02	[88Kle]
$\beta$ -Mo <sub>2</sub> N <850°	tI12 I4 <sub>1</sub> /and Mo <sub>2</sub> N	a= 420. c= 801.	[85Vil]

$\gamma\text{-Mo}_2\text{N}$ <1950°	oF8 Fm $\bar{3}$ m NaCl-defect	a= 418.5	[85Vil]
$\delta\text{-MoN}$	hP18 P6 <sub>3</sub> /mmc MoN	a= 572.5 c= 560.8	[85Vil] >0.085 GPa
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]

Table 2: Thermodynamic data for the system Mo-B-N

Phase	$\Delta_f G$ ( J/granatom )		Ref.
1.0000 Mo	$\Delta_{fus} G(\text{Mo})$	= 37479.8-12.942 T	[88Spe
1.0000 B	$\Delta_{fus} G(\text{B})$	= 50210-21.23 T	
1.0000 Mo	$\Delta_f G(\text{Mo})$	= 0	
0.3333 Mo <sub>2</sub> B	$\Delta_f G(\text{Mo}_2\text{B})$	= -42860+2.43 T	
0.5000 MoB	$\Delta_f G(\text{MoB})$	= -53170+0.47 T	
0.3769 MoB <sub>1.053</sub>	$\Delta_f G(\text{MoB}_{1.053})$	= -45690-0.22 T	
0.3170 MoB <sub>2.155</sub>	$\Delta_f G(\text{MoB}_{2.155})$	= -50940+4.27 T	
0.2079 MoB <sub>~9.81</sub>	$\Delta_f G(\text{MoB}_{~9.81})$	= -34107+3.13 T	
1.0000 $\beta\text{B}$	$\Delta_f G(\beta\text{B})$	= 0	
Liquid(Mo,B)	$\Delta G^{ex} = x(1-x)\{-148435+10.90 T + 21000(1-2x)+25305(1-2x)^2\}$		
0.3333 Mo <sub>2</sub> N	$\Delta_f G(\text{Mo}_2\text{N})$	= -19107.4+17.97 T	[76Fro]

Fig.1: The binary system Mo - B; based on [65Rud,77Sto] and [88Kle].

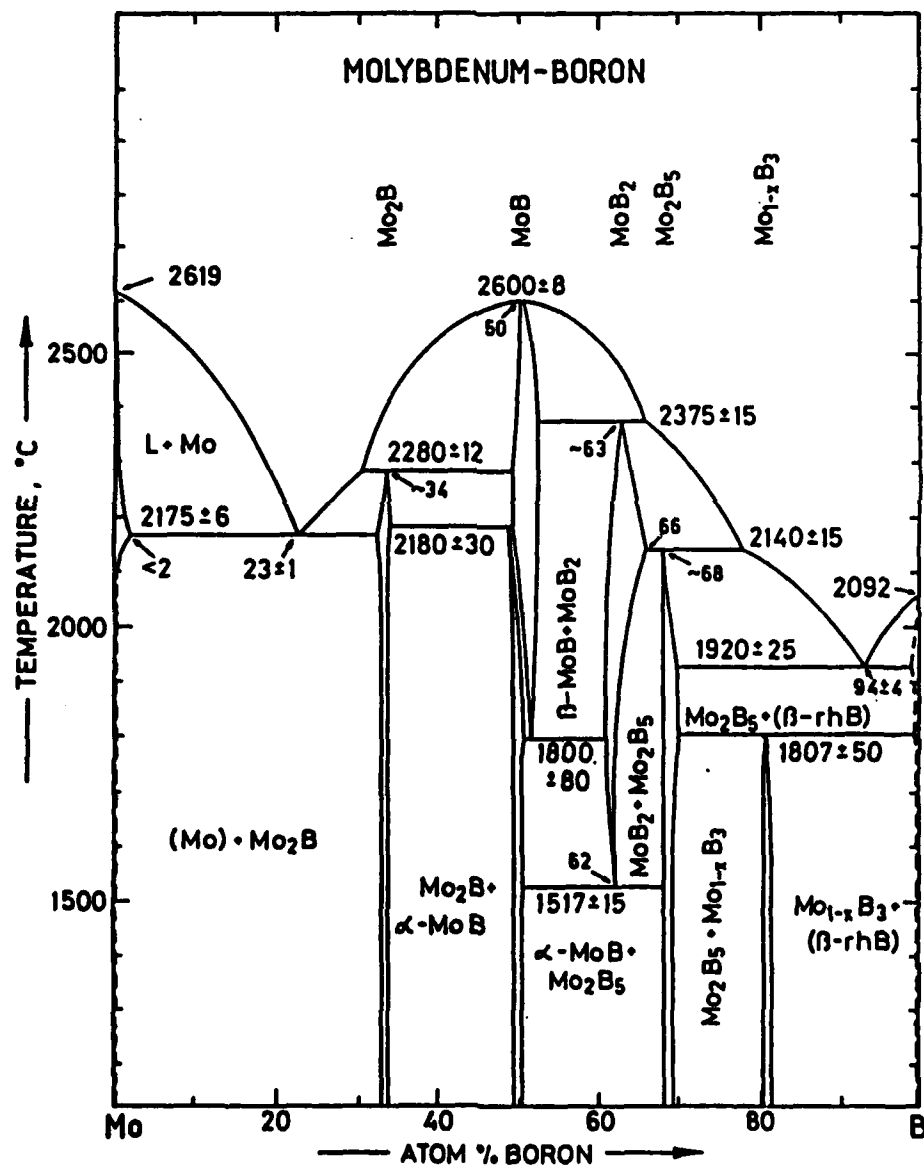


Fig.2: Isothermal section at 1200°C in the system Mo - B - N under Ar (in the absence of external nitrogen)

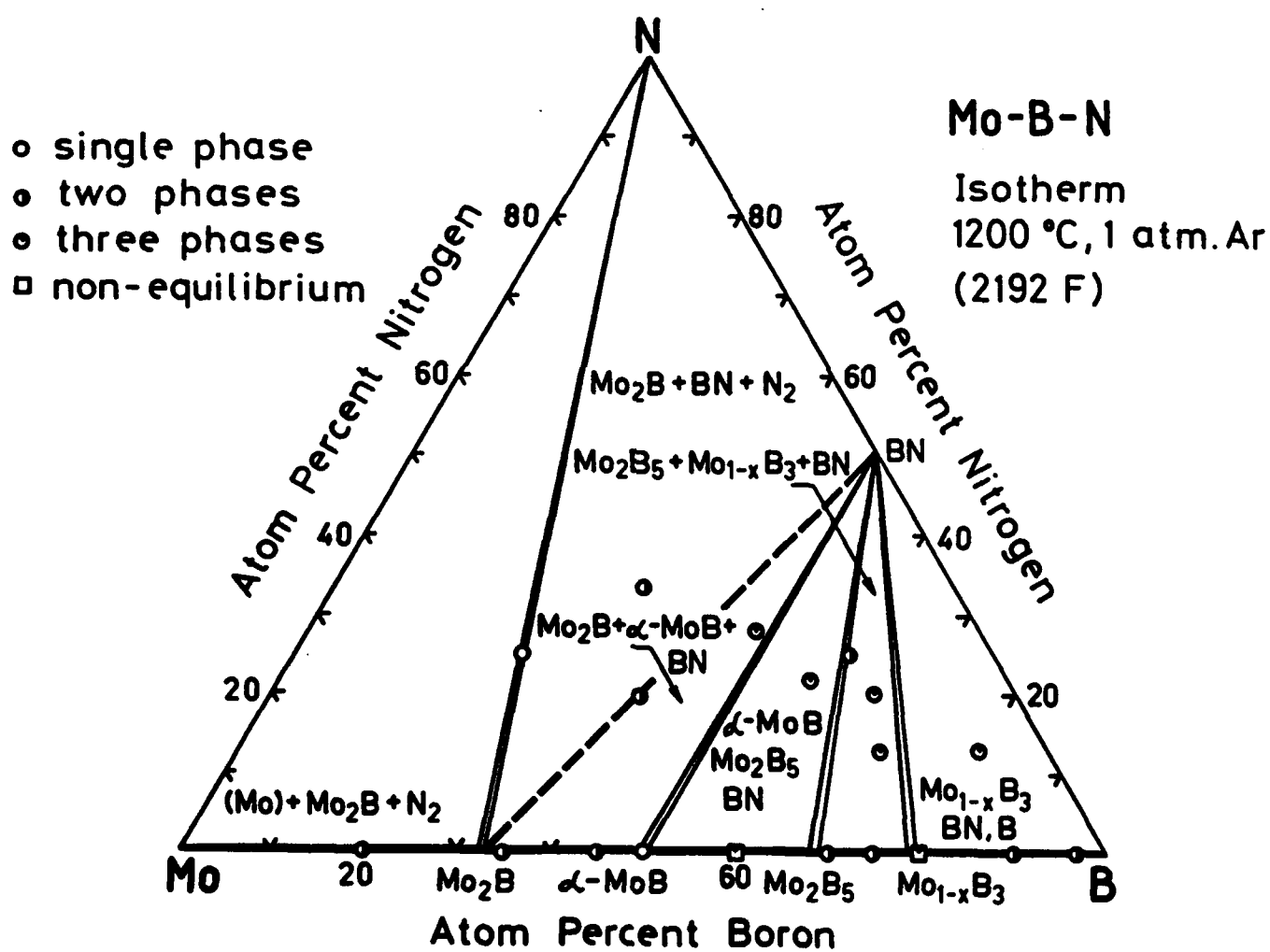


Fig.3: Isothermal section at 1400°C in the system Mo - B - N under Ar (in the absence of external nitrogen)

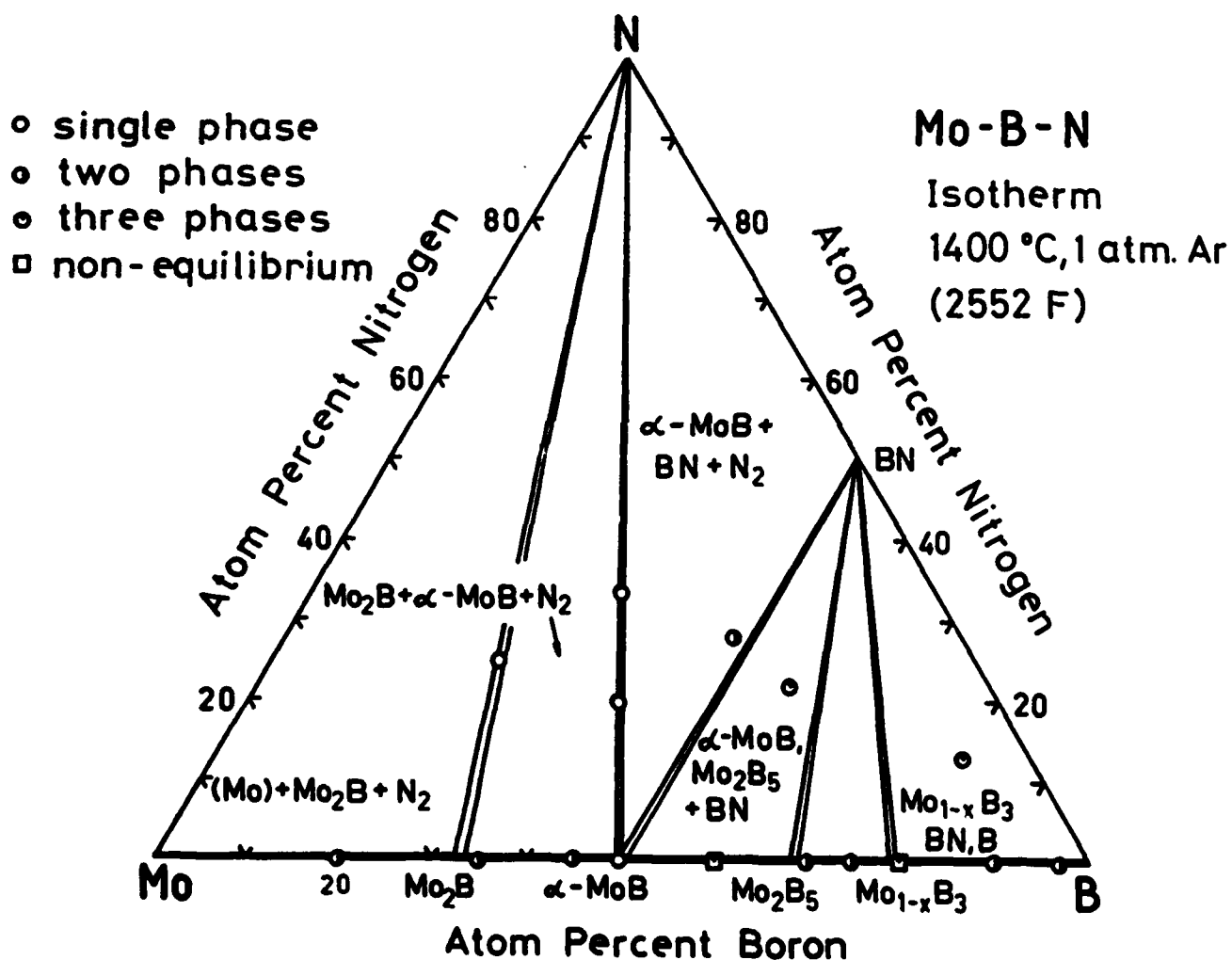
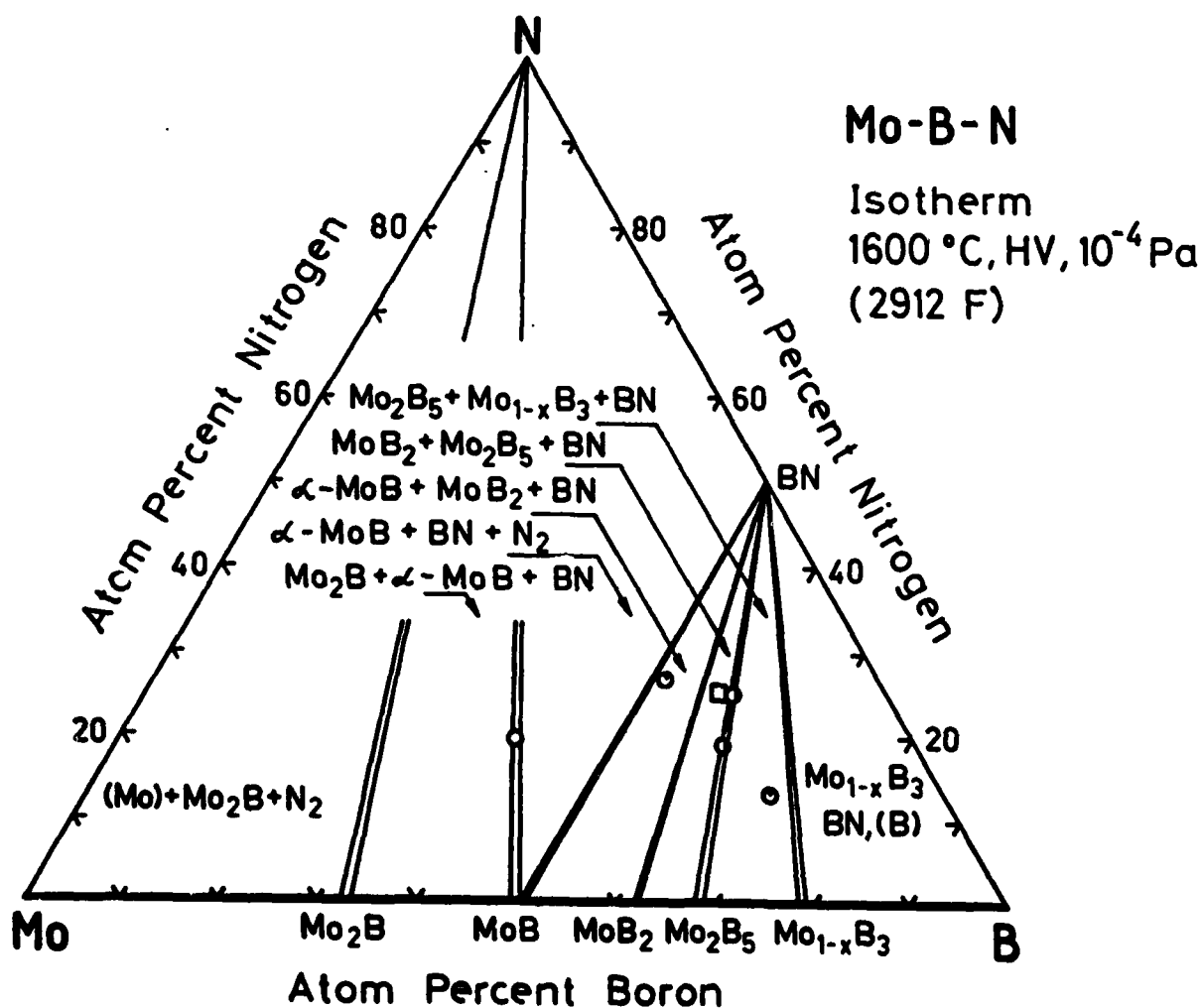


Fig.4: Isothermal section at 1600°C in the system Mo - B - N under Ar. (in the absence of external nitrogen)





## SYSTEM BORON- TUNGSTEN - NITROGEN (B-W-N)

### INTRODUCTION / EXPERIMENTAL

Informations on the W-B-N ternary are due to [51Kis], [69Bae1,2] (see section *Thermodynamics*) and [88Kle].

The thermal stability of the binary tungsten borides was investigated in a dry stream of ammonia at temperatures below 1100°C by [51Kis]. The resistance against attack by ammonia was found to increase with the boron content and no mutual solid solubility was observed [51Kis].

Phase equilibria in the B-W-N system have been established at 1200°, 1400°, and 1600°C from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, W, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20  $\mu$ m in a steel mortar and/or a WC-Co mortar respectively [88Kle]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N<sub>2</sub>) usually consisted of a primary reaction at 1200°C for 96h followed by a final reaction at 1200°C (or 1400°, 1600°C respectively) for up to 70h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Starting materials were powders of 3N-W, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [88Kle].

### BINARY SYSTEMS

The reinvestigation of the B-W system in the range from 1200 to 1600°C revealed consistency with the data available in [84Vil], and [90Mas]. The maximal solid solubility of boron in tungsten was claimed to be less than 1 at%B at the W-W<sub>2</sub>B eutectic temperature (2800°C); an interstitial type of B-solubility was suggested [65Rud]. The maximum solid solubility of W in  $\beta$ -B was reported to be less

than 0.5 at% W at  $\sim 1800^{\circ}\text{C}$  [85Rud] in agreement with X-ray data by [81Cre] (see Table 1). Fig.1 is a representation of the constitutional diagram W-B.

No phase diagram is available for the system W-N ; a critical assessment is due to [89Wri]. The binary tungsten nitrides are unstable at  $T > 1000^{\circ}\text{C}$  and  $p(\text{N}_2) < 10^5 \text{ Pa}$  [89Wri]. A detailed discussion of solubility data , physical properties and thermodynamic data is found in [76Fro].

#### SOLID PHASES / ISOTHERMAL SECTIONS

Figs.2-4 represent the isothermal sections at  $1200^{\circ}\text{C}$ ,  $1400^{\circ}\text{C}$  and  $1600^{\circ}\text{C}$  under 1 bar of argon (in the absence of external nitrogen pressure) [88Kle]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between the higher tungsten borides and BN. Phase equilibria were found to be rather dependent on the nitrogen partial pressure. The stability of the (W + BN)- and the ( $\text{W}_2\text{B}$  + BN)-two phase equilibria as a function of T and  $p(\text{N}_2)$  were investigated [88Kle] in good agreement to earlier data by [51Kis], [69Bae1,2] and confirm the observed phase equilibria ( see also section *Thermodynamics* ). Thus at  $1200$  and  $1400^{\circ}\text{C}$  and under 1 bar Ar (W + BN) decomposes to  $\text{W}_2\text{B}$  +  $\text{N}_2$  , and similarly at higher temperatures ( $1600^{\circ}\text{C}$ ) the subboride  $\text{W}_2\text{B}$  becomes incompatible with BN and decomposes under formation of WB +  $\text{N}_2$  [88Kle]. Phase equilibria were furthermore checked at  $1400^{\circ}\text{C}$  applying a vacuum of  $10^{-4} \text{ Pa}$  for 100h revealing a rapid decomposition of (W+BN) starting compositions into  $\text{W}_2\text{B}$ , WB, and WB+BN [88Kle]. The kinetic of nitriding binary tungsten borides was studied at  $1200$  and  $1400^{\circ}\text{C}$  under 1 bar of  $6\text{N-N}_2$  and confirmed the phase equilibria in Figs.2-4 [88Kle].

As seen from a comparison of the unit cell dimensions there is no significant solid solubility of W in BN up to  $1000^{\circ}\text{C}$ , and mutual solubilities of the tungsten borides and BN up to  $1600^{\circ}\text{C}$  are rather restricted [88Kle].

## THERMODYNAMICS

A calculation of the W-B binary system was attempted by [84Kau]; see Table 2.

[69Bae1,2] studied the reaction of W and BN using a Thermobalance. From these measurements the activation energies for the formation of the binary borides were derived. Furthermore the onset of the reaction  $2\text{W} + \text{BN} \rightleftharpoons \text{W}_2\text{B} + 1/2\text{N}_2$  was measured as a function of the nitrogen partial pressure yielding free enthalpy data for the reaction and data for the free enthalpy of formation for  $\text{W}_2\text{B}$ .

## REFERENCES

- [51Kis] R.Kiessling and Y.H.Liu , "The Thermal Stability of The Chromium, Iron, and Tungsten Borides In Streaming Ammonia and The Existence of a New Tungsten Nitride" Trans.AIME -J.Metals 3 (1951) 639-642
- [65Rud] E.Rudy and S.Windisch, " The System Molybdenum - Boron ", AFML-Technical Report 2, Part I, Vol.III, Wright Patterson Air Force Base, Ohio (1965) pp. 1-72
- [69Bae1] F.D.Baehren and D.Vollath, "A Determination of The Thermodynamic Data of The Borides  $\text{Mo}_2\text{B}$ ,  $\text{W}_2\text{B}$  and  $\text{Re}_3\text{B}$ " (in German), Planseeber.f.Pulvermetall., 17 (1969) 180-183
- [69Bae2] F.D.Baehren, F.Thuennler and D.Vollath, "The Kinetics of The Formation of The Borides of Mo, W and Re from Boron Nitride-Metal Powder Mixtures" (in German), J. Less-Common Metals, 18 (1969) 295-303
- [76Fro] E. Fromm, and E.Gebhardt, "Gases and Carbon in Metals" (Springer, Berlin, 1976)
- [81Cre] A.J.Crespo, L.E.Tergenius and T.Lundstroem, "The Solid Solution of  $\delta$ ,  $\epsilon$  and Some p Elements in  $\beta$ -rh Boron", J. Less-Common Metals, 77 (1981) 147-150
- [84Kau] L.Kaufman, B.Uhrenius, D.Birnie and K. Taylor, "Coupled Pair Potential, Thermochemical and Phase Diagram Data for Transition Metal Binary Systems-VII", CALPHAD 8 (1984) 25-66
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, Oh, 1985)
- [88Kle] H.Klesnar and P.Rogl "Phase Relations in The Ternary System :Tungsten - Boron - Nitrogen", research at the Univ. Vienna, (1988) ,to be published
- [89Wri] H.A.Wriedt, "The W-N System", Bull. Alloy Phase Diagram 10 (1989) 358-367
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., Amer.Soc.Met., Metals Park, Oh, 1990.

Table 1: Solid phases in the system B-W-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
W <3422°	cI2 Im $\bar{3}m$ W	a= 316.52	[80Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}m$ $\beta$ -B	a=1092.51 c=2381.43 a=1093.82 c=2383.56	[85Vil] [85Vil] [81Cre] at 0.5at%W
W <sub>2</sub> B <2670°	tI12 I4/mcm Al <sub>2</sub> Cu	a= 556.50 c= 474.32	[88Kle]
$\alpha$ -WB <2170°	tI16 I4 <sub>1</sub> /and $\alpha$ -MoB	a= 310.09 c=1695.6	[88Kle]
$\beta$ -WB <2665°	oC8 Cmcm CrB	a= 314.2 b= 850.6 c= 306.5	[85Rud]
W <sub>2</sub> B <sub>5</sub> <2365°	hP14 P6 <sub>3</sub> /mmc W <sub>2</sub> B <sub>5</sub>	a= 298.45 c=1387.3	[88Kle]
W <sub>1-x</sub> B <sub>5</sub> <2020°	hP P6 <sub>3</sub> /mmc W <sub>1-x</sub> B <sub>5</sub>	a= 519.76 c= 633.51	[88Kle]
W <sub>2</sub> N	cF8 Fm $\bar{3}m$ NaCl	a= 412.6	[85Vil]
$\delta$ -WN	hP2 P $\bar{6}m2$ WC	a= 289.3 c= 282.6	[85Vil]

BN<sub>hex</sub>

hP\*

a= 250.4

[85Vil]

P<sub>g</sub>/mmc

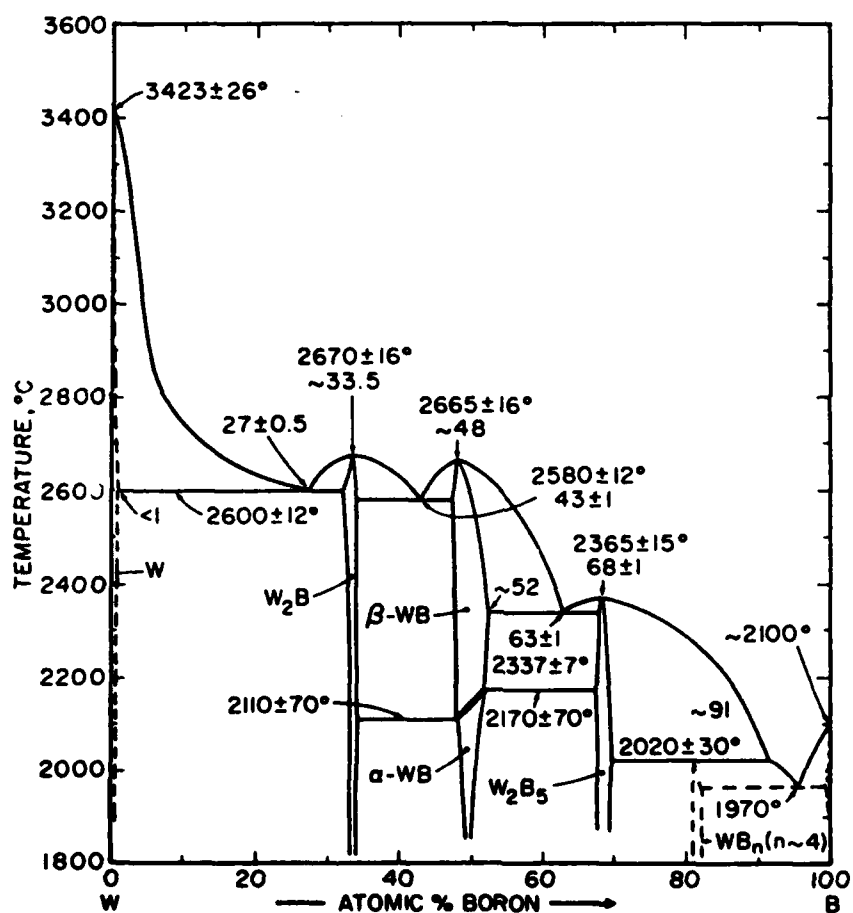
c= 888.1

BN<sub>hex</sub>

Table 2: Thermodynamic data for the system W-B-N

Phase	$\Delta_f G$ ( J/gramatom )	Ref.
1.0000 W	$\Delta_{fus} G(W) = 52313.69 - 14.158 T$	[84Kau]
1.0000 B	$\Delta_{fus} G(B) = 50210 - 21.23 T$	
1.0000 W	$\Delta_f G (W) = 0$	
0.3333 W <sub>2</sub> B	$\Delta_f G (W_2B) = -41783 + 1.406 T$	
0.5000 WB	$\Delta_f G (WB) = -54392 + 1.125 T$	
0.7140 W <sub>2</sub> B <sub>3</sub>	$\Delta_f G (W_2B_3) = -55229 + 2.564 T$	
0.8000 WB <sub>4</sub>	$\Delta_f G (WB_4) = -41840 + 2.075 T$	
1.0000 $\beta B$	$\Delta_f G (\beta B) = 0$	
Liquid(W,B)	$\Delta G^{ex} = x(1-x)\{-75312 - 215058 x - 8.368 T\}$	

Fig.1: The binary system W - B; based on [85Rud]



[illegible]



Fig.3: Isothermal section at 1400°C in the system W - B - N under Ar (in the absence of external nitrogen)

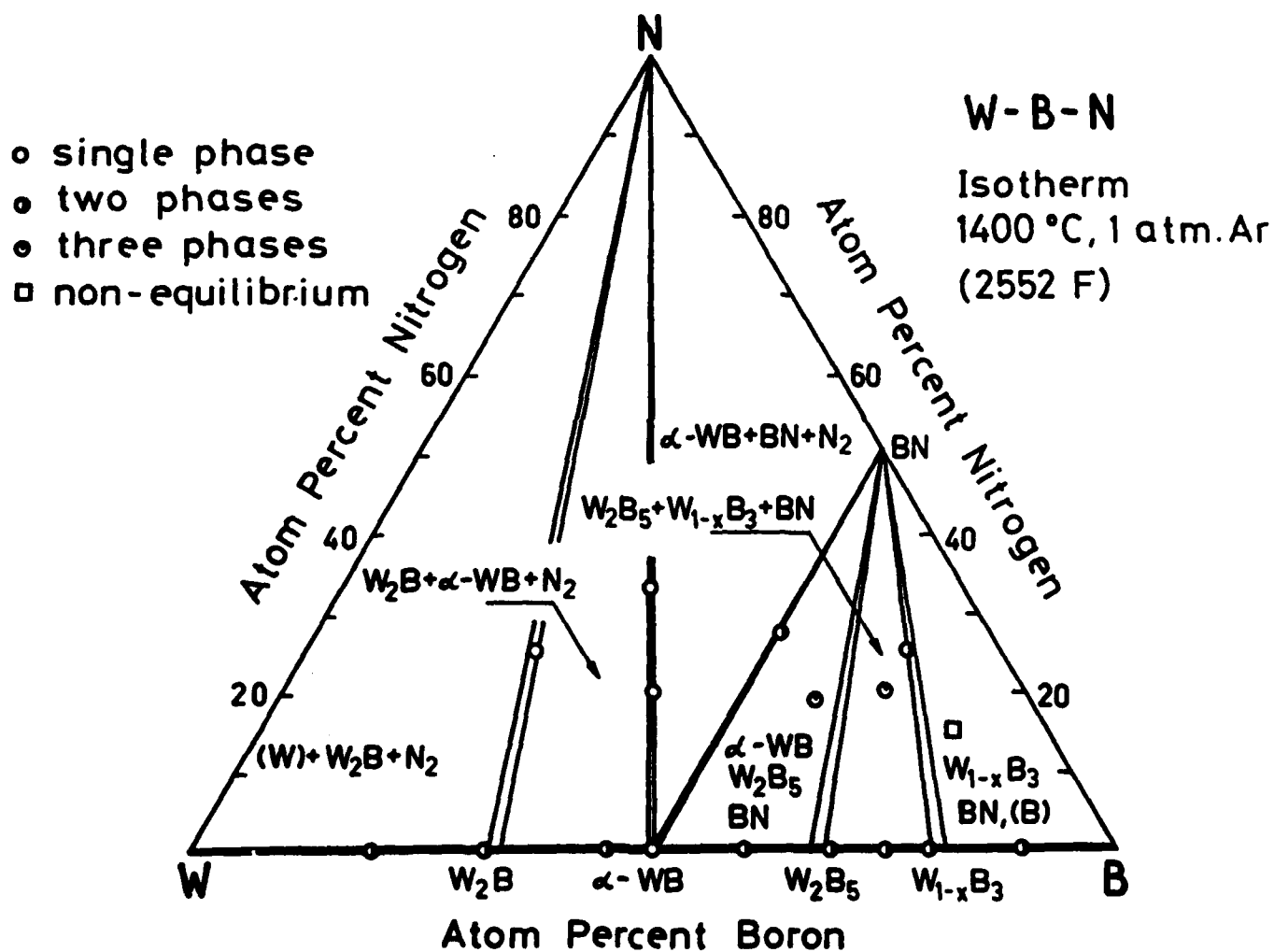
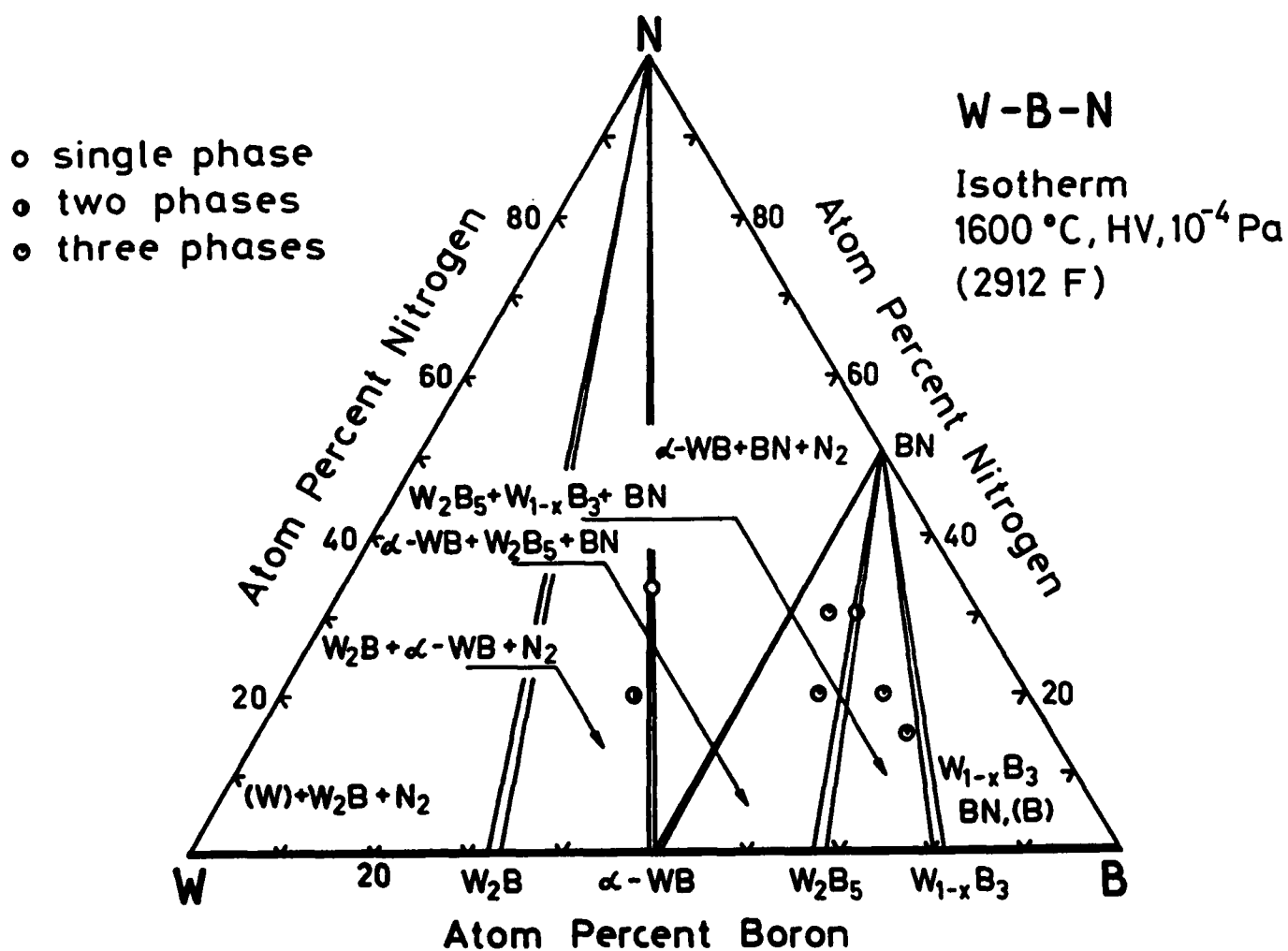


Fig.4: Isothermal section at 1800°C in the system W - B - N under Ar (in the absence of external nitrogen)



## SYSTEM BORON- MANGANESE- NITROGEN (B-Mn-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Mn-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, Mn,  $Mn_2N$ , and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than  $20\mu m$  in a steel mortar and/or a WC-Co mortar respectively [89<sup>V</sup>Sm]. Annealing of the samples was either performed (a) in vacuum sealed silica tubes using a thin molybdenum foil to protect the sample from direct contact with the hot quartz wall or (b) in a 1 MHz-HF furnace under 1 bar of 5N-Ar or under various partial pressures of 5N- $N_2$  using hex-BN substrates in a tungsten or molybdenum susceptor crucible. Heat treatments usually consisted of a primary reaction at  $900^\circ C$  for 72 to 120h followed by a final reaction at  $900^\circ C$  up to 700h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were either monitored by calibrated microoptical pyrometry or by thermocouples; after heat treatment the samples were radiation cooled ( HF-furnace ) or quenched in water ( silica capsules ). Some of the samples were quenched in liquid nitrogen. In-situ high temperature X-ray data were recorded under Ti-gettered He using a W-sheet metal substrate and Au-powder as internal standard [89<sup>V</sup>Sm].

The starting materials were powders from 3N-Mn plates, surface cleaned in dilute HCl prior to use, powders of 99 %  $Mn_2N$ , crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at  $1400^\circ C$ . Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth or by direct sintering under argon; weight losses were checked to be within 1 wt% [89<sup>V</sup>Sm].

### BINARY SYSTEMS

The reinvestigation of the B-Mn system from as-cast alloys and in the range from 800 to  $1250^\circ C$  confirmed the existence of six binary

manganese borides [89<sup>V</sup>Mi]. In contrast to earlier data there is essential consistency with the data available from a recent compilation by [86Lia]. The low temperature modification of  $\alpha$ -MnB was unambiguously revealed to be CrB-type from X-ray diffractometry of single crystals grown by iodine vapour transport [89<sup>V</sup>Mi]. Homogeneous ranges of the binary borides at 900°C were found to be rather small except for MnB<sub>2</sub> indicating a typical "line-compound" type of character. The solid solubility of boron in the various allotropes of manganese (interstitial type) was claimed to be less than 0.5 to 1.0 at%B. From X-ray powder analysis the maximum solid solubility of Mn in  $\beta$ -B was concluded to be about 4.2 at%Mn at 1800°C. An extensive discussion of the Mn-B phase diagram has been recently published by [89<sup>V</sup>Mid]; for crystallographic data see Table 1. Fig.1 represents the critically assessed version of the Mn-B phase diagram, temperature versus concentration [89<sup>V</sup>Mi].

The reinvestigation of the phase relations in the Mn-rich part of the Mn-N diagram [89<sup>V</sup>Mi] revealed consistency with a critical assessment of the Mn-N diagram as presented by [90Gok]. It shall be mentioned, however, that the formation of the so-called  $\delta'$ -phase ( bct. martensitic transformation from the fcc-(Mn,N)  $\gamma$ -phase ) was observed in all samples quenched from 900°C in water [89<sup>V</sup>Mi].

The maximum solid solubility of N in Mn was said to be smaller than 0.5 at% N for  $\alpha$ -Mn, 2 at% N for  $\beta$ -Mn and 11 at% N for  $\gamma$ -Mn at 790°C [90Gok].

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.2 represent the isothermal section at 900°C under 1 bar of argon (in the absence of external nitrogen pressure) [89<sup>V</sup>Mi]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between manganese and the binary manganese-borides and BN. As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Mn in BN at 900°C, and mutual solubilities of the manganese nitrides, the manganese borides and BN are rather restricted [89<sup>V</sup>Mi]. Due to insufficient quenching, the Mn<sub>4</sub>N-phase is present in the 900°C section.

Phase equilibria in the Mn,N-rich region of the ternary system

are rather dependent on the nitrogen partial pressure. According to the thermodynamic stability of the binary manganese nitrides, prolonged heating of  $\zeta$ - $\text{Mn}_2\text{N}$  at  $900^\circ\text{C}$  in a dynamic vacuum of  $3 \cdot 10^{-4}\text{Pa}$  resulted in a successive decomposition into lower nitrides (after 40 h) towards the nitrogen rich end of the (Mn) solid solution (after 80 h). In all ternary samples which had been reacted at  $900^\circ\text{C}$  under  $10^{-5}\text{Pa}$   $\text{N}_2$  prior to heat treatment in high vacuum, the (Mn) solid solution and all manganese borides revealed compatibility with respect to  $\text{BN}_{\text{hex}}$ . The reaction paths as well as the distribution of the phase fields at  $900^\circ\text{C}$  and under a high vacuum are presented in Fig.3.

X-ray analysis of alloys representing the (Mn + BN) twophase equilibrium which subsequently were held for 1 h at  $1350^\circ\text{C}$  under Ar, revealed instability with respect to decomposition into (Mn) +  $\text{Mn}_2\text{B}$  +  $\text{N}_2$ .

A detailed discussion of the phase relations in the Mn-B-N ternary is found in [89Šmi].

#### THERMODYNAMICS

A thermodynamic modelling of the binary system Mn-B is due to [88Lia] including a critical assessment of earlier attempts to calculate the phase diagram; see Table 2.

#### REFERENCES

- [78Fro] E. Fromm, H. Jehn and G. Hoerz, "Gases and Carbon in Metals" ZAE, Physics Data, 5-3 (1978) pp 2
- [85Vil] P. Villars and L.D. Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, Oh, 1985)
- [88Lia] P.K. Liao and K.E. Spear, "The B-Mn (Boron-Manganese) System", Bull. Alloy Phase Diagr. 7 (1986) 543
- [89Šmi] I. Šmid, P. Rogl and F. Weitzer, "The Ternary System Manganese - Boron - Nitrogen", Proceedings of the 12<sup>th</sup> Int. Plansee Seminar (H. Bildstein and H. Ortner Eds.) Tyrolia, Innsbruck, Austria, Vol 2 (1989) 577-598

[98Gok] N.A.Gokcen, "The Phase Transformations in Mn", Bull. Alloy Phase Diagrams 10 (1989) 313

[90Gok] N.A.Gokcen, "The Mn-N (Manganese-Nitrogen) System", Bull. Alloy Phase Diagrams 11 (1990) 33

Table 1: Solid phases at 900°C in the system B-Mn-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\alpha$ -Mn <727°	cI58 I $\bar{4}$ 3m $\alpha$ -Mn	a= 891.39	[90Gok] at RT [89Gok]
$\beta$ -Mn 1100-727°	cP20 P4 <sub>1</sub> 32 $\beta$ -Mn	a= 631.51	[90Gok] at RT [89Gok]
$\gamma$ -Mn 1138-1100°	cF4 Fm $\bar{3}$ m $\gamma$ -Mn	a= 386.3	[90Gok] at 1100°C [89Gok]
$\delta$ -Mn 1246-1138°	cI2 Im $\bar{3}$ m W	a= 308.1	[90Gok] at 1136°C [89Gok]
$\beta$ -rhB	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
$\alpha$ -Mn <sub>2</sub> B <~1285°	oF40 Fddd $\alpha$ -Mn <sub>2</sub> B	a=1099.07 c=2399.64 a=1455.7 b= 728.7 c= 420.7	[85Vil] at MnB <sub>23</sub> [89 <sup>V</sup> Smi]
t-Mn <sub>2</sub> B <1580°	tI12 I4/mcm Al <sub>2</sub> Cu	a= 514.8 c= 420.4	[89 <sup>V</sup> Smi]
$\alpha$ -MnB <1050°	oP8 Cmcm	a= 302.34 b= 767.59	[89 <sup>V</sup> Smi]

	CrB	c= 295.68		
$\beta$ -MnB	oP8	a= 414.8	[89 <sup>V</sup> mi]	
1890-1050°	Pbnm	b= 555.6		
	FeB	c= 297.7		
Mn <sub>3</sub> B <sub>4</sub>	oI14	a= 303.4	[89 <sup>V</sup> mi]	
<1750°	Immm	b=1282.2		
	Ta <sub>3</sub> B <sub>4</sub>	c= 296.3		
MnB <sub>2</sub>	hP3	a= 300.89	[86Lia]	
1990-1075°	P6/mmm	c= 303.84		
	AlB <sub>2</sub>			
MnB <sub>4</sub>	mC14	a= 548.5	[89 <sup>V</sup> mi]	
<1375°	C2/m	b= 537.5		
	MnB <sub>4</sub>	c= 294.5		
		$\beta$ =122.47°		
$\delta'$ -(Mn,N)	tI2	a= 267.2	[89 <sup>V</sup> mi]	
	I4/mmm	c= 355.0		
Mn <sub>4</sub> N	cP5	a= 382.7	[89 <sup>V</sup> mi]	
<890°	Fm $\bar{3}$ m			
	Fe <sub>4</sub> N			
$\beta$ -Mn <sub>2</sub> N <sub>1-x</sub>	hP3	a= 276.73	[89 <sup>V</sup> mi]	
	P6 <sub>3</sub> /mmc	c= 452.12		
	Fe <sub>2</sub> N			
$\alpha$ -Mn <sub>2</sub> N <sub>1-x</sub>	hP12	a= 489.16	[89 <sup>V</sup> mi]	
	P6 <sub>3</sub> 22	c= 455.45		
	Mn <sub>2</sub> N <sub>0.88</sub>			
Mn <sub>2</sub> N	oP12	a= 485.52	[89 <sup>V</sup> mi]	
	C222 <sub>1</sub>	b= 840.88		
	Mn <sub>2</sub> N	c= 453.27		
Mn <sub>2</sub> N	oP12	a= 566.8	[89 <sup>V</sup> mi]	
	Pbna	b= 490.9		
	Mo <sub>2</sub> C	c= 453.7		
hP-Mn <sub>3</sub> N <sub>2</sub>	tI8	a= 297.4	[89 <sup>V</sup> mi]	at 0.6 GPa
	I4/mmm	c=1212.6		400°C
	ThH <sub>2</sub>			
$\alpha$ -Mn <sub>6</sub> N <sub>5</sub>	tI4	a= 298.02	[89 <sup>V</sup> mi]	at 47.9at%N
<410°	I4/mmm	c= 414.8		
	NaCl-deriv.			

$\beta\text{-Mn}_5\text{N}_3$ >410°	cF8 Fm $\bar{3}$ m NaCl	a= 422.5	[89 <sup>V</sup> Smi]
BN <sub>hex</sub>	hP5 P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 886.1	[85Vil]

Table 2: Thermodynamic data for the system Mn-B (after [86Lia])

Phase	$\Delta_f G$ ( J/granaton )	Ref.
1.0000 Mn	$\Delta_{fus} G(\text{Mn}) = 12908.94 - 8.4984 T$	[86Lia]
1.0000 B	$\Delta_{fus} G(\text{B}) = 50210 - 21.23 T$	
1.0000 $\alpha\text{Mn}$	$\Delta_f G(\alpha\text{Mn}) = 0$	
1.0000 $\beta\text{Mn}$	$\Delta_f G(\beta\text{Mn}) = 1908.32 - 1.3525 T$	
0.3333 Mn <sub>2</sub> B	$\Delta_f G(\text{Mn}_2\text{B}) = -31254 + 0.293 T$	
0.5000 MnB	$\Delta_f G(\text{MnB}) = -36225 + 0.439 T$	
0.1429 Mn <sub>3</sub> B <sub>4</sub>	$\Delta_f G(\text{Mn}_3\text{B}_4) = -27396 - 2.050 T$	
0.3333 MnB <sub>2</sub>	$\Delta_f G(\text{MnB}_2) = -21902 - 2.040 T$	
0.2000 MnB <sub>4</sub>	$\Delta_f G(\text{MnB}_4) = -26098 + 6.582 T$	
1.0000 $\beta\text{B}$	$\Delta_f G(\beta\text{B}) = 0$	
Liquid	$\Delta G^{ex} = x(1-x)\{-179800 + 41.73 T - 29273(1-2x) + 74194(1-2x)^2 + 66081(1-2x)^3 - 52134(1-2x)^4\}$	
0.2000 Mn <sub>4</sub> N	$\Delta_f G(\text{Mn}_4\text{N}) = -4534 + 3.266 T$	[75Gme]
0.3333 Mn <sub>2</sub> N	$\Delta_f G(\text{Mn}_2\text{N}) = -83667.7 + 5.807 T$	[75Gme]
0.2000 Mn <sub>3</sub> N <sub>2</sub>	$\Delta_f G(\text{Mn}_3\text{N}_2) = -6680 + 5.696 T$	[75Gme]



Fig.1: Assessed diagram of the binary system Mn - B

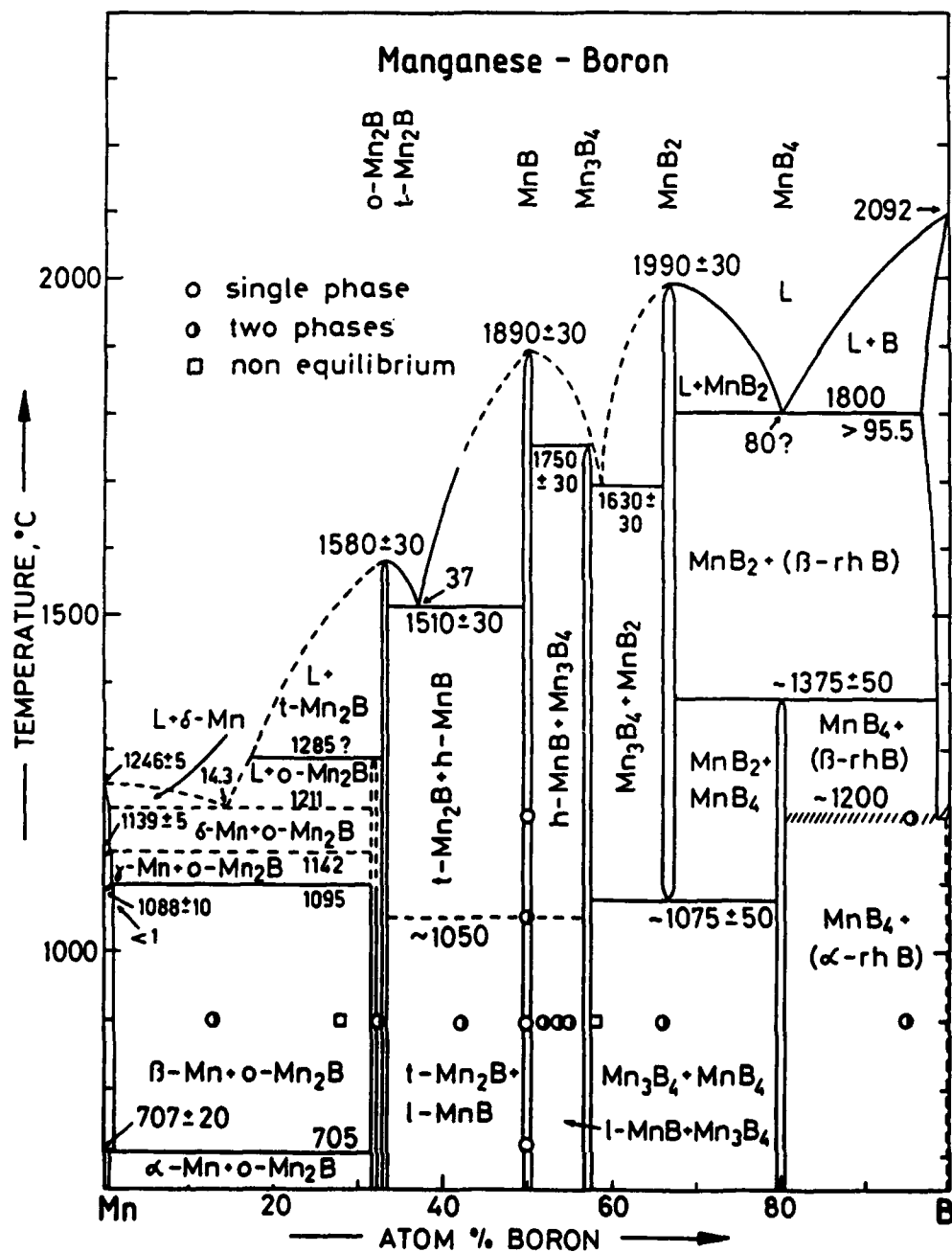


Fig.2: Isothermal section of the system B - Mn -N at 900°C under 1 bar of argon ( in the absense of external nitrogen ).

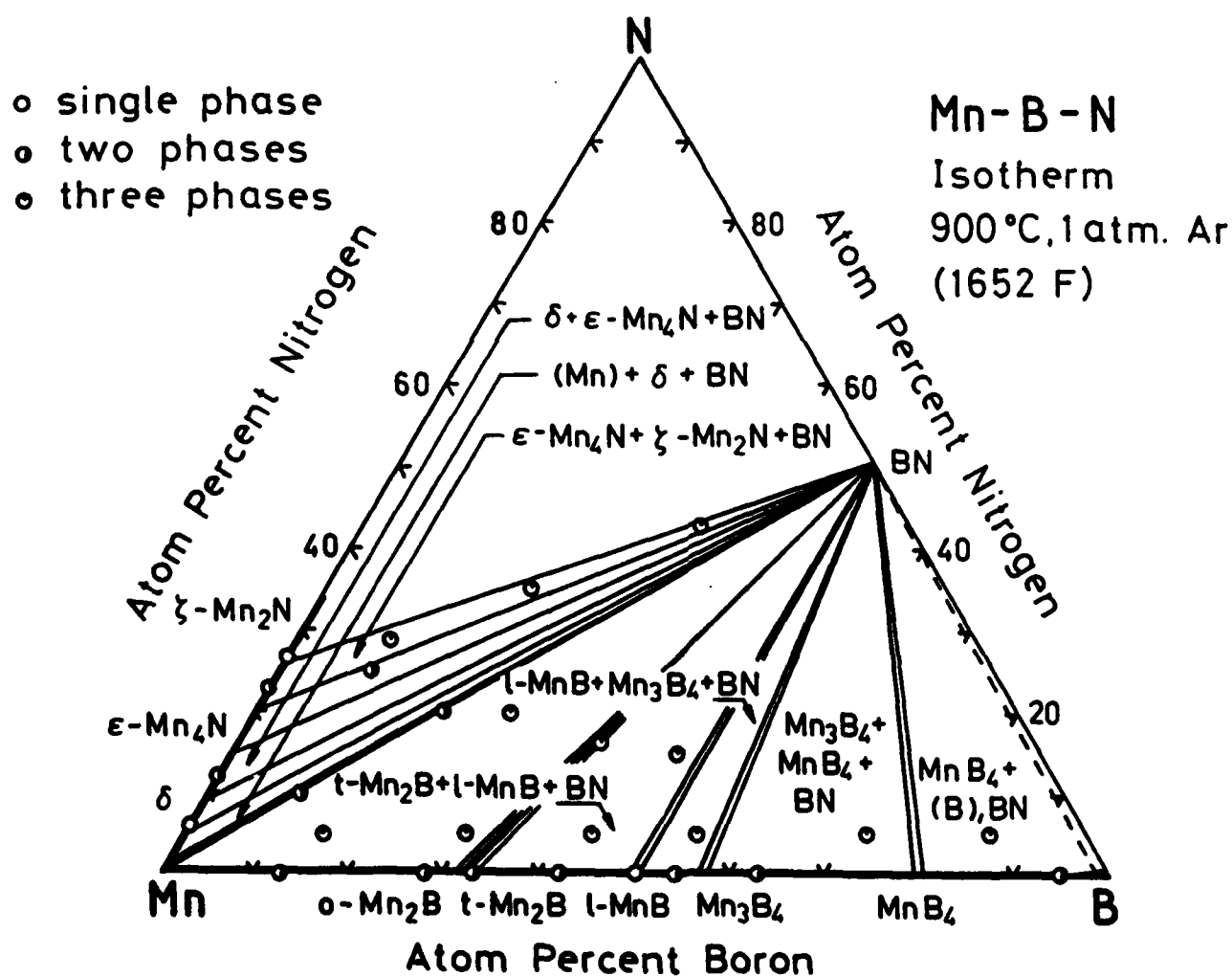
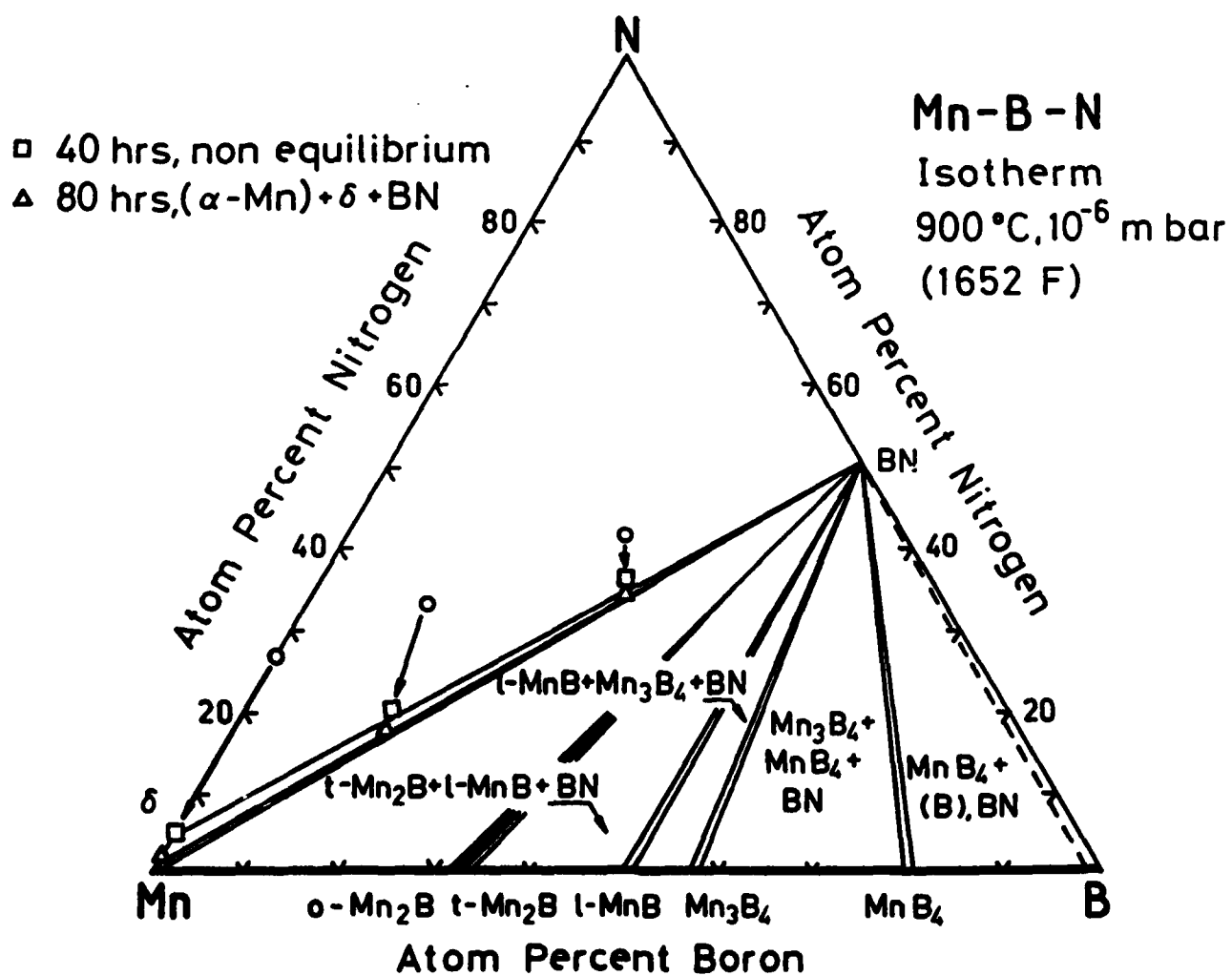


Fig.3 Isothermal section of the system B - Mn - N at 900°C under a vacuum of  $10^{-4}$  Pa.



## SYSTEM BORON- RHENIUM- NITROGEN (B-Re-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Re-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, Re, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than  $20\mu\text{m}$  in a steel mortar and/or a WC-Co mortar respectively [88Rog]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace (under 1 bar of 5N-Ar or 5N-N<sub>2</sub>) usually consisted of a primary reaction at 1200°C for 24h followed by a final reaction at 1200°C for 84h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Re, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [88Rog].

### BINARY SYSTEMS

The reinvestigation of the B-Re system in the range from 1200 to 1500°C revealed consistency with the data available in [84Vil] and [90Mas]; see Table 1. Due to the rather sluggish diffusion reactions in the high melting B-Re system, thermodynamic equilibrium at 1200°C was not attained in those alloys which were arc melted prior to heat treatment at 1200°C. In correspondance to the observations by [88Por], a weak set of X-ray reflections was observed in the rhenium-rich alloys which was concluded to belong to a new Re-boride labelled as Re<sub>s-x</sub>B, whose crystal structure is still unknown [88Rog]. Homogeneous ranges of the binary borides at 1200°C were found to be rather small indicating a typical "line-compound" type of character.

The solid solubility of boron in rhenium was claimed to be less than 2 at%B at the temperature of the peritectic formation of Re<sub>3</sub>B (

ca 2150°C); an interstitial type of B-solubility was suggested [65Trz]. The maximum solid solubility of Re in  $\beta$ -B was reported to be less than 1 at%Re at 1800°C [81Cre].

No equilibrium diagram exists for the N-Re system and solid solubility of N in Re is said to be small ( $10^{-2}$  at%N at  $10^5$  Pa); only one binary nitride,  $\text{ReN}_{1-x}$  (cF8,  $Fm\bar{3}m$ , defect NaCl-type,  $a=0.393\text{nm}$  at 30 at%N), exists, but decomposes in vacuum below 270°C; a comprehensive discussion of all reported information has been given by [78Fro].

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 1200°C under 1 bar of argon (in the absence of external nitrogen pressure) [88Rog]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between rhenium metal and/or the binary rhenium-borides and BN. As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Re in BN at 1200°C, and mutual solubilities of the rhenium borides and BN are rather restricted [88Rog].

Phase equilibria in the Re-B-N system have been also checked by nitriding the binary rhenium boride powders under 1 bar of  $\text{N}_2$ . The results confirm the gradual decomposition of the higher borides via lower borides towards a limiting tie-line: (Re) + BN. No signs of compound formation at higher nitrogen contents were observed.

## THERMODYNAMICS

[69Bae1,2] studied the reaction of Re and BN using a Thermobalance. From these measurements the activation energies for the formation of the binary borides were derived. Furthermore the onset of the reaction  $3\text{Re} + \text{BN} \rightleftharpoons \text{Re}_3\text{B} + 1/2\text{N}_2$  was measured as a function of the nitrogen partial pressure yielding free enthalpy data for the reaction and data for the free enthalpy of formation for  $\text{Re}_3\text{B}$ .

## REFERENCES

- [65Trz] W.Trzebiatowski and J.Berak, " Bull.Acad.Polon.Sci. Cl.III, Vol.II (1965) 37
- [68Por] K.I.Portnoi and B.T.Romashov," The Phase Diagram of the Re-B System", Poroshkov. Metall. 62 (1968) 41-44
- [69Bae1] F.D.Baehren and D.Vollath, "Determination of the Thermodynamic Data of the Borides  $\text{Mo}_2\text{B}$ ,  $\text{W}_2\text{B}$  and  $\text{Re}_3\text{B}$ " (in German), Planseeber.f.Pulvermetall., 17 (1969) 180-183
- [69Bae2] F.D.Baehren, F.Thuennler and D.Vollath, " The Kinetics of the Formation of the Borides of Mo, W, and Re from Boron Nitride Metal Powder Mixtures", J. Less-Common Metals, 18 (1969) 195
- [78Fro] E. Fromm, H. Jehn and G. Hoerz, "Gases and Carbon in Metals" ZAED, Physics Data, 5-3 (1978) pp 2
- [81Cre] A.J.Crespo, L.E.Tergenius and T.Lundstroem, "The Solid Solution of 4d, 5d and some p Elements in  $\beta$ rh. Boron", J. Less-Common Metals, 77 (1981) 147-150
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, Oh, 1985)
- [88Rog] P.Rogl and C.Horvath "Phase Relations in The Ternary System :Rhenium - Boron - Nitrogen", research at the Univ. Vienna, (1988), to be published
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met., Metals Park, Oh, 1990)

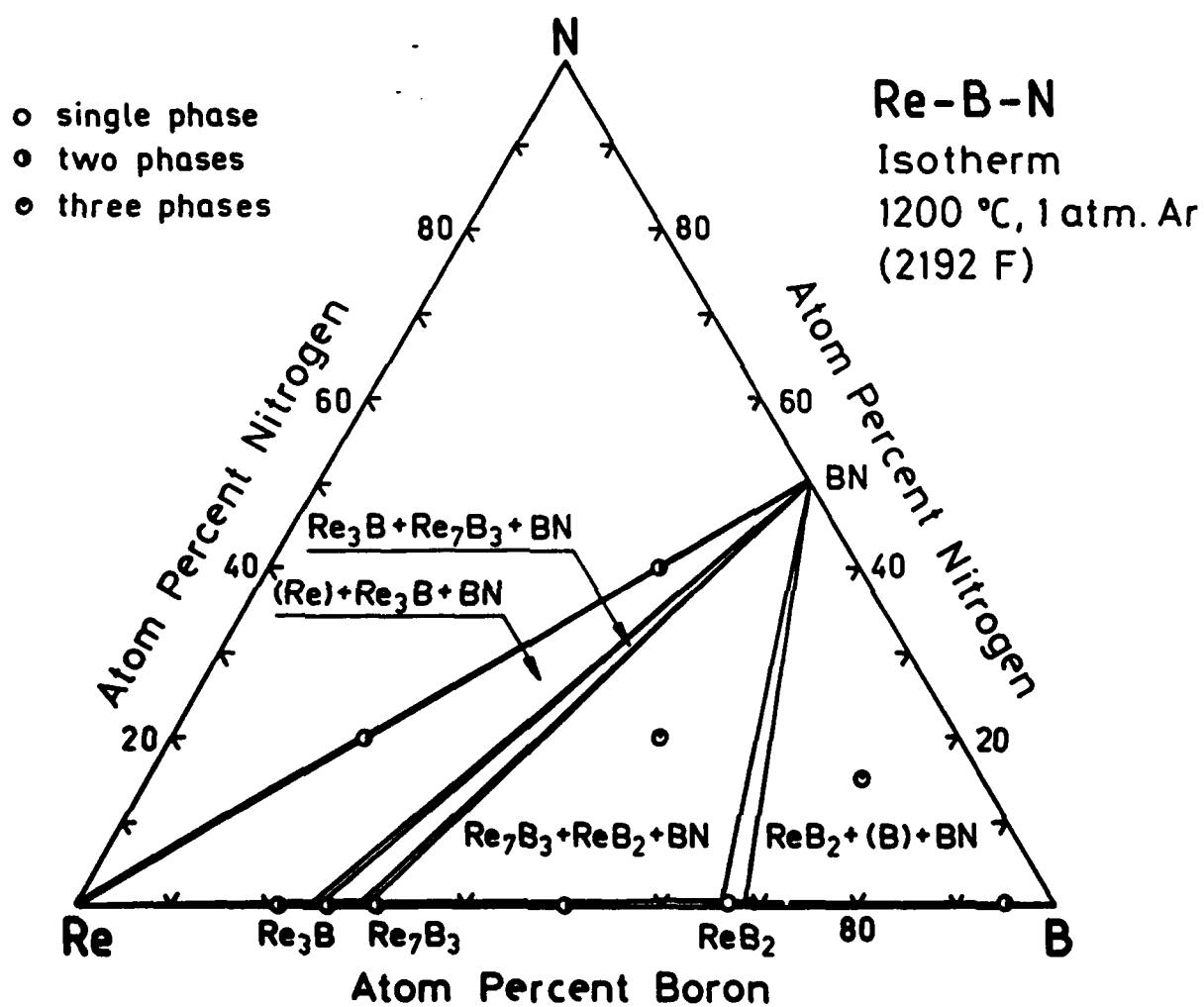
Table 1: Solid phases at 1200°C in the system B-Re-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Re <3186°	hP2 P6 <sub>3</sub> /mmc Mg	a= 276.09 c= 445.8	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
Re <sub>3</sub> B ~2150°	oC16 Cmcm Re <sub>3</sub> B	a= 289.33 b= 932.08 c= 727.08	[88Rog]
Re <sub>7</sub> B <sub>3</sub> <~2000°	hP20 P6 <sub>3</sub> mc Th <sub>7</sub> Fe <sub>3</sub>	a= 750.48 c= 488.54	[88Rog]
ReB <sub>2</sub> <~2400°	hP6 P6/mmc ReB <sub>2</sub>	a= 290.16 c= 747.99	[88Rog]
BN <sub>hex</sub>	hP5 P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]

Table 2: Thermodynamic data for the system Re-B-N

Phase	$\Delta_f G$ ( J/gramaton )	Ref.
1.0000 Re	$\Delta_{fus} G(\text{Re}) = 80428 - 17.4698 T$	
1.0000 B	$\Delta_{fus} G(\text{B}) = 50210 - 21.23 T$	
1.0000 Re	$\Delta_f G(\text{Re}) = 0$	
0.2500 Re <sub>3</sub> B	$\Delta_f G(\text{Re}_3\text{B}) = -32320 + 7.32 T$	[69Bae]
1.0000 $\beta$ B	$\Delta_f G(\beta\text{B}) = 0$	

Fig.1: Isothermal section of the system B - Re -N at 1200°C under 1 bar of argon ( in the absense of external nitrogen ).





## SYSTEM BORON- IRON- NITROGEN (B-Fe-N)

### INTRODUCTION / EXPERIMENTAL

Early information on the Fe-B-N system is due to [51Kis] who investigated the stability of binary iron borides in a stream of dry ammonia at temperatures between 352 and 768°C. The resistance against attack by ammonia was found to increase with the boron content; no mutual solid solubility was observed [51Kis] confirming earlier findings by [48Jac].

The solubility of nitrogen in iron-rich alloys ( 0.001 to 0.91 wt% B ) has been studied by [62Fou] using Sievert's technique in the temperature range from 950 to 1150°C. Small amounts of desoxidising Si yielded a total of 0.5 wt% Si in the alloy whose effect on the N-solubility was determined from B-free samples. A TEM-study of extracted flakes of (BN<sub>hex</sub>) revealed a lack of threedimensional perfection due to stacking faults and random displacement of the graphitic layers perpendicular to the c-axis, but with (hk0) reflections unaffected [62Fou]. At 1050°C the mutual solid solubilities of Fe - BN and Fe<sub>2</sub>B - BN were said to be very small [62Fou].

The N-solubility limit in liquid Fe-B alloys was investigated by [64Eva] using ( a ) Sievert's technique and ( b ) equilibration of iron melts in BN crucibles under a constant partial pressure of N<sub>2</sub>. Boron was found to decrease the N-solubility at a given partial pressure of N<sub>2</sub> and the first order interaction coefficient, determined between 1550 and 1750°C [64Eva], was expressed as a function of temperature by [74Sig] :  $\epsilon = 975/T - 0.4$  ( T in K ). Based on the results of [64Eva] and following a similar procedure the saturation phase boundaries L/(L + BN) have been calculated by [87Rag] for 1550, 1650, 1750°C and for 1, 5 and 10.10<sup>5</sup> Pa N<sub>2</sub>.

Phase equilibria in the B-Fe-N system at 900°C have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, Fe, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20µm in a steel mortar and/or a WC-Co mortar respectively [85Sm], [86Sm]. Annealing of the samples was either performed (a) in vacuum sealed silica tubes using a thin

molybdenum foil to protect the sample from direct contact with the hot quartz wall or (b) in a 1 MHz-HF furnace under 1 bar of 6N-Ar or under various partial pressures of 6N-N<sub>2</sub> using hex-BN substrates in a tungsten or molybdenum susceptor crucible. Heat treatments usually consisted of a primary reaction at 900°C for 48h followed by a final reaction at 900°C up to 72h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were either monitored by calibrated microoptical pyrometry or by thermocouples; after heat treatment the samples were radiation cooled ( HF-furnace ) or quenched in water ( silica capsules ). The starting materials were powders from 3N-Fe , crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements or by direct sintering under argon; weight losses were checked to be within 1 wt% [85<sup>V</sup>Smi, 86<sup>V</sup>Smi].

#### BINARY SYSTEMS

The reinvestigation of the B-Fe system from 400°C to the melting range employing X-ray powder, metallographic, DTA, and Pirani-melting point analyses confirmed the existence of only two binary iron borides [86Smi]. In contrast to earlier data there is essential consistency with the data available from a compilation by [82Kub]. In contradiction to a low temperature modification " $\alpha$ -FeB" as claimed earlier ( for a review see [82Kan]), FeB-samples containing excess boron at temperatures below  $T \sim 1000^\circ\text{C}$  revealed a typical transposition type behavior (FeB-type ---- CrB-type) with an irregular arrangement of the FeB-type slabs in partly shifted positions but without long range order [85<sup>V</sup>Smi, 86<sup>V</sup>Smi]. The maximal solid solubility of boron in  $\alpha$ -Fe was said to be small, whereas detailed measurements of the electrical resistivity and the activity coefficients of B in  $\alpha, \gamma$ -Fe reveal a solubility of B in  $\gamma$ -Fe, which is 2.7 times larger than that in  $\alpha$ -Fe at the same temperature [83Bro]. While there seems to be no doubt about the interstitial type of B-solubility in  $\gamma$ -Fe, a substitutional mode was discussed for  $\alpha$ -Fe by [84Hay]. From X-ray powder analysis the maximum solid solubility of Fe in  $\beta$ -B was concluded to be about 5 at% Fe at 1800°C. An extensive discussion of the Fe-B phase diagram can be found from [85Smid, 86Smi] including a

discussion on the metastable phases  $\text{Fe}_{23}\text{B}_6$  and  $\text{Fe}_3\text{B}$ ; for crystallographic data see Table 1. A thermodynamic modelling of the Fe-B system is due to [87<sup>V</sup>Sm].

Fig.1 represents the critically assessed version of the Fe-B phase diagram, temperature versus concentration [86<sup>V</sup>Sm].

The phase diagram Fe-N is due to critical assessments by [76Fro], [82Kub], [87Wri], [87Fri] and [86Kun].

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.2 summarizes the results reported by [51Kis] in terms of an isothermal section at 400°C (in the absence of external nitrogen pressure). Fig.3 shows the phase equilibria in the iron rich corner of the Fe-B-N system at 950, 1050, and 1150°C as derived by [62Fou]. Fig.4 represents the phase relations in the Fe-B-N system at 900°C [85<sup>V</sup>Sm, 86<sup>V</sup>Sm]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between iron and the binary iron-borides and BN. As seen from a comparison of the unit cell dimensions there is a small but significant solid solubility of Fe in BN at 900°C, whereas mutual solubilities of the iron nitrides, the iron borides and BN are rather restricted [85<sup>V</sup>Sm]. Alloys along the section Fe-BN with a composition of about 20 mol % BN after heat treatment at 1350°C and 1 bar argon were reported to be molten and after quenching revealed the powder pattern of a cubic  $\tau$ -phase  $\text{Fe}_{23}(\text{B},\text{N})_6$ . Technical conditions - using graphite susceptor crucibles and technical argon containing 0.01 %  $\text{O}_2$ , 0.02 %  $\text{N}_2$  at 900°C and 48 h prompted the stabilization of a  $\text{Fe}_3(\text{B},\text{N},\text{C})$  compound with the  $\text{Fe}_3\text{C}$ -type [86<sup>V</sup>Sm] ( Fig.5).

The kinetic of nitriding was studied [86<sup>V</sup>Sm] from binary iron boride samples annealed at 900 and 1250°C under 1 bar of 6N-nitrogen and qualitatively confirmed the early observations by [51Kis].

## THERMODYNAMICS

A thermodynamic modelling of the binary system Fe-B is due to [86Sm] of the Fe-N system due to [87Fri]; see Table 2.

## REFERENCES

- [78Fro] E. Fromm, H. Jehn and G. Hoerz, "Gases and Carbon in Metals" ZAED, Physics Data, 5-3 (1978) pp 2
- [85Vil] P. Villars and L.D. Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, Oh, 1985)
- [48Jac] K.H. Jack, "The Iron Nitrogen System: the Structures of  $\text{Fe}_4\text{N}$  and  $\text{Fe}_2\text{N}$ ", Proc. R. Soc. (London) 195A (1948) 34-40
- [51Kis] R. Kiessling and Y.H. Liu, "Thermal Stability of the Cr, Fe, and W Borides in Streaming Ammonia and The Existence of a New Tungsten Nitride", Trans AIME-J. Met., N.Y. 3 (1951) 639-642
- [62Fou] R.W. Fountain and J. Chipman, "Solubility and Precipitation of Boron Nitride in Iron Boron Alloys", Trans. AIME 224 (1962) 599
- [64Eva] D.B. Evans and R.D. Pehlke, "The Boron-Nitrogen Equilibrium in Liquid Iron", Trans. AIME 230 (1964) 1657-1662
- [64Hay] Y. Hayashi and T. Sugeno, J. Phy. Soc. Japan 19 (1964) 1252
- [74Sig] G.K. Sigworth and J.F. Elliott, "The Thermodynamics of Liquid Dilute Iron Alloys", Met. Sci. J. 8 (1972) 298-310
- [82Kan] T. Kanaizuka, "Phase Diagram of Pseudobinary CrB-MnB and MnB-FeB Systems: Crystal Structure of the Low Temperature Modification of FeB", J. Solid State Chem. 41 (1982) 195-204
- [82Kub] O. Kubaschewski-von Goldbeck, (Ed.) "Iron Binary Phase Diagrams" Springer-Verlag, Berlin (1982) 15-18
- [83Bro] H. Brodowsky and H.J. Wernicke, Calphad XII Liege, (1983)
- [85Šmi] I. Šmid and P. Rogl, "Phase Equilibria and Structural Chemistry in Ternary Systems: Transition Metal - Boron Nitrogen", Proceedings of the 11<sup>th</sup> Intl. Plansee Seminar (H. Bildstein and H. Ortner Eds.) Tyrolia, Innsbruck, Austria, Vol 2 (1985) 1029-1035
- [86Šmi] I. Šmid and P. Rogl, "Phase Equilibria and Structural Chemistry in Ternary Systems: Transition Metal-Boron-Nitrogen", Inst Phys. Conf. Ser. No. 75: Chapter 4, Adam Hilger Ltd. (1986) 249-257
- [86Kun] J. Kunze, "Thermodynamic Calculation of Phase Diagrams in the Iron-Nitrogen System", Steel Res. 57 (1986) 361-367

[87Fri] K.Frisk, "A New Assessment of the Fe-N Phase Diagram", CALPHAD 11(2) (1987) 127-134

[87Wri] H.A.Wriedt, N.A.Gokcen and R.H.Nafziger, "The Fe-N (Iron-Nitrogen) System", Bull.Alloy Phase Diagrams 8(4) (1987) 355-377

Table 1: Solid phases in the system B-Fe-N

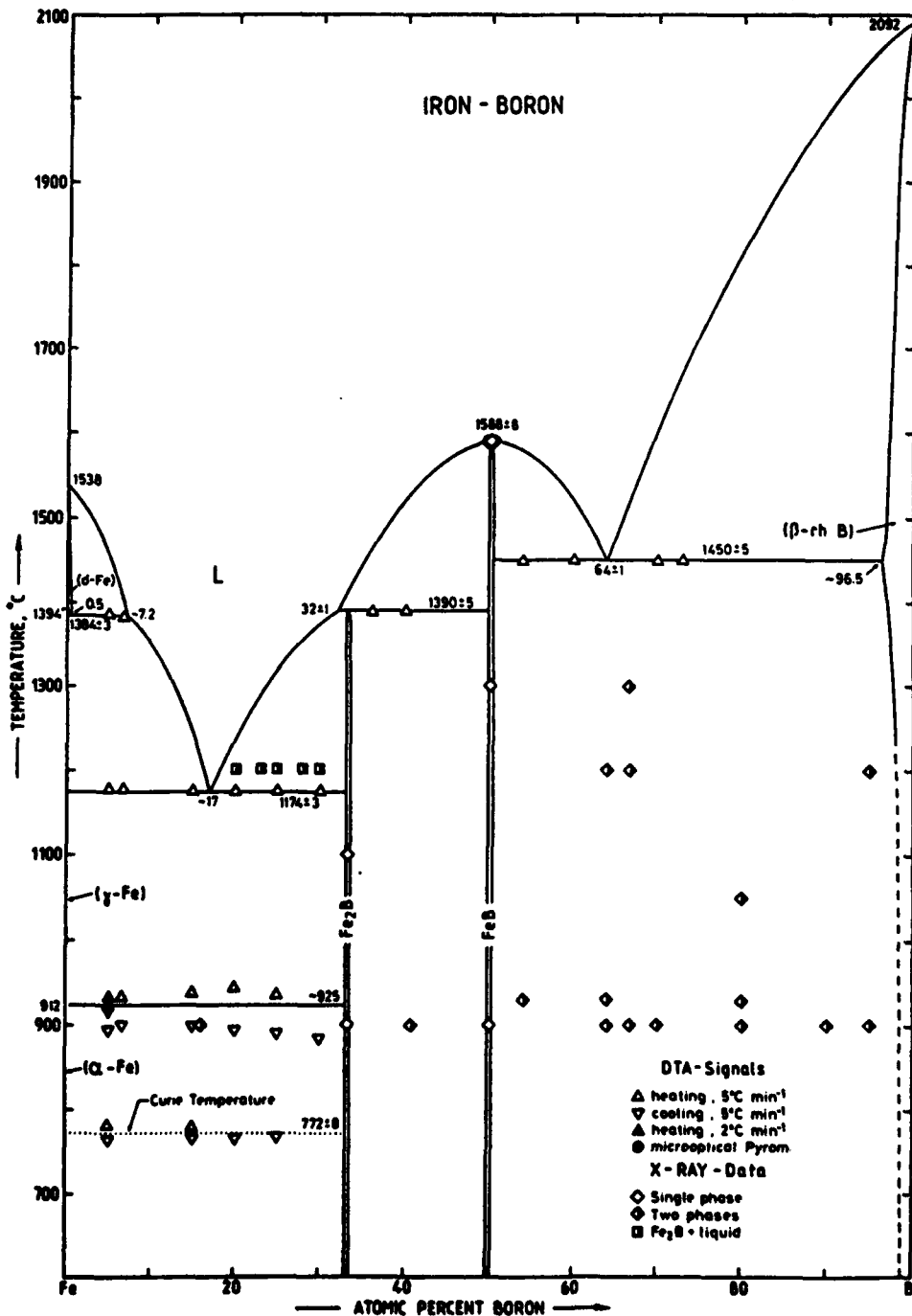
Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\alpha$ -Fe <912°	cI2 Im $\bar{3}$ m W	a= 286.65 a= 294.1	[87Wri] at RT [87Wri] at 1538°C
$\gamma$ -Fe <1394°	cF4 Fm $\bar{3}$ m Cu	a= 364.7 a= 368.8	[87Wri] at 912°C [87Wri] at 1394°C
$\delta$ -Fe <1535°	cI2 Im $\bar{3}$ m W	a= 293.15	[85Vil]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
		a=1095.14 c=2386.1	[85Vil] at FeB <sub>49</sub>
Fe <sub>2</sub> B <1174°	tI12 I4/mcm Al <sub>2</sub> Cu	a= 510.9 c= 424.9	[85Vil]
FeB <1588°	oP8 Pbnm FeB	a= 406.1 b= 550.6 c= 295.2	[85Vil]
Fe <sub>23</sub> B <sub>6</sub>	cF116 Fm $\bar{3}$ m Cr <sub>23</sub> C <sub>6</sub>	a=1067.	[85Vil] metastable

$\text{Fe}_3\text{B}$	$\text{oP16}$	$a = 443.9$	[85Vil]	metastable
	$\text{Pbnm}$	$b = 542.8$		
	$\text{Fe}_3\text{C}$	$c = 866.9$		
$\text{Fe}_3\text{B}$	$\text{tI32}$	$a = 865.5$	[85Vil]	metastable
	$\text{I}\bar{4}$	$c = 429.7$		
$\text{Fe}_3\text{B}$	$\text{Fe}_3\text{P}$		[85Vil]	metastable
	$\text{tP32}$	$a = 864.8$		
	$\text{P4}_2/\text{n}$	$c = 431.4$		
$\text{Fe}_4\text{N}$ <680°	$\text{Ti}_3\text{P}$		[87Wri]	at 20 at% N
	$\text{cP5}$	$a = 379.8$		
	$\text{Pn}\bar{3}\text{m}$			
$\text{Fe}_3\text{N}_{1-x}$	$\text{Fe}_4\text{N}$		[87Wri]	at 20 at% N
	$\text{hP9}$	$a = 435.3 + 1.337(\text{at}\% \text{N})$		
	$\text{P31m}$	$c = 423.3 + 0.578(\text{at}\% \text{N})$		
$\text{Fe}_2\text{N}$ <480°	$\text{Fe}_3\text{N}$		[87Wri]	15.8-33.2 at% N [87Rag]
	$\text{oP12}$	$a = 551.2$		
	$\text{Pbcn}$	$b = 482.0$		
$\text{Fe}_3\text{N}$	$\text{Fe}_2\text{N}$	$c = 441.6$	[87Wri]	11.1 at% N metastable
	$\text{tI}$	$a = 572.$		
	$\text{I4/mmm}$	$c = 629.$		
$\text{BN}_{\text{hex}}$	$\text{Fe}_3\text{N}$		[85Vil]	
	$\text{hP5}$	$a = 250.4$		
	$\text{P6}_3/\text{mmc}$	$c = 866.1$		
$\text{BN}_{\text{hex}}$	$\text{BN}_{\text{hex}}$		[85Vil]	
	$\text{cF116}$			
	$\text{Pn}\bar{3}\text{m}$			
$*\text{Fe}_{23}(\text{B}, \text{N})_6$	$\text{Cr}_{23}\text{C}_6$		[85Vil]	metastable
	$\text{oP16}$	$a = 1048.3$		
	$\text{Pbnm}$			
$*\text{Fe}_3(\text{B}, \text{N}, \text{C})$	$\text{Fe}_3\text{C}$	$a = 445.9$	[85Vil]	C-stabil.
	$\text{oP16}$	$b = 534.7$		
	$\text{Pbnm}$	$c = 866.4$		

Table 2: Thermodynamic data for the system Fe-B (after [86<sup>V</sup>ni])

Phase	$\Delta_f G$ ( J/granaton )	Ref.
1.0000 Fe	$\Delta_{f,us} G(\text{Fe}) = 13806 - 7.6241 T$	[86 <sup>V</sup> ni]
1.0000 B	$\Delta_{f,us} G(\text{B}) = 50210 - 21.23 T$	
1.0000 $\alpha\text{Fe}$	$\Delta_f G (\alpha\text{Fe}) = 0$	
1.0000 $\gamma\text{Fe}$	$\Delta_f G (\gamma\text{Fe}) = 825.78 - 0.4953 T$	
0.3333 $\text{Fe}_2\text{B}$	$\Delta_f G(\text{Fe}_2\text{B}) = -102330 + 5.0 T$	
0.0769 FeB	$\Delta_f G(\text{FeB}) = -36980 + 2.0 T$	
1.0000 $\beta\text{B}$	$\Delta_f G (\beta\text{B}) = 0$	
Liquid	$\Delta G^{ex} = x(1-x)\{-177050 - 34.9 T + (-3335 + 68.9 T)(1-2x)\}$	

**Fig.1: Assessed diagram of the binary system Fe - B [85<sup>V</sup>ni,86<sup>V</sup>ni]**





**Fig.2: Isothermal section of the system B - Fe -N at 400°C ( in the absense of external nitrogen ) as based on data by [51Kis].**

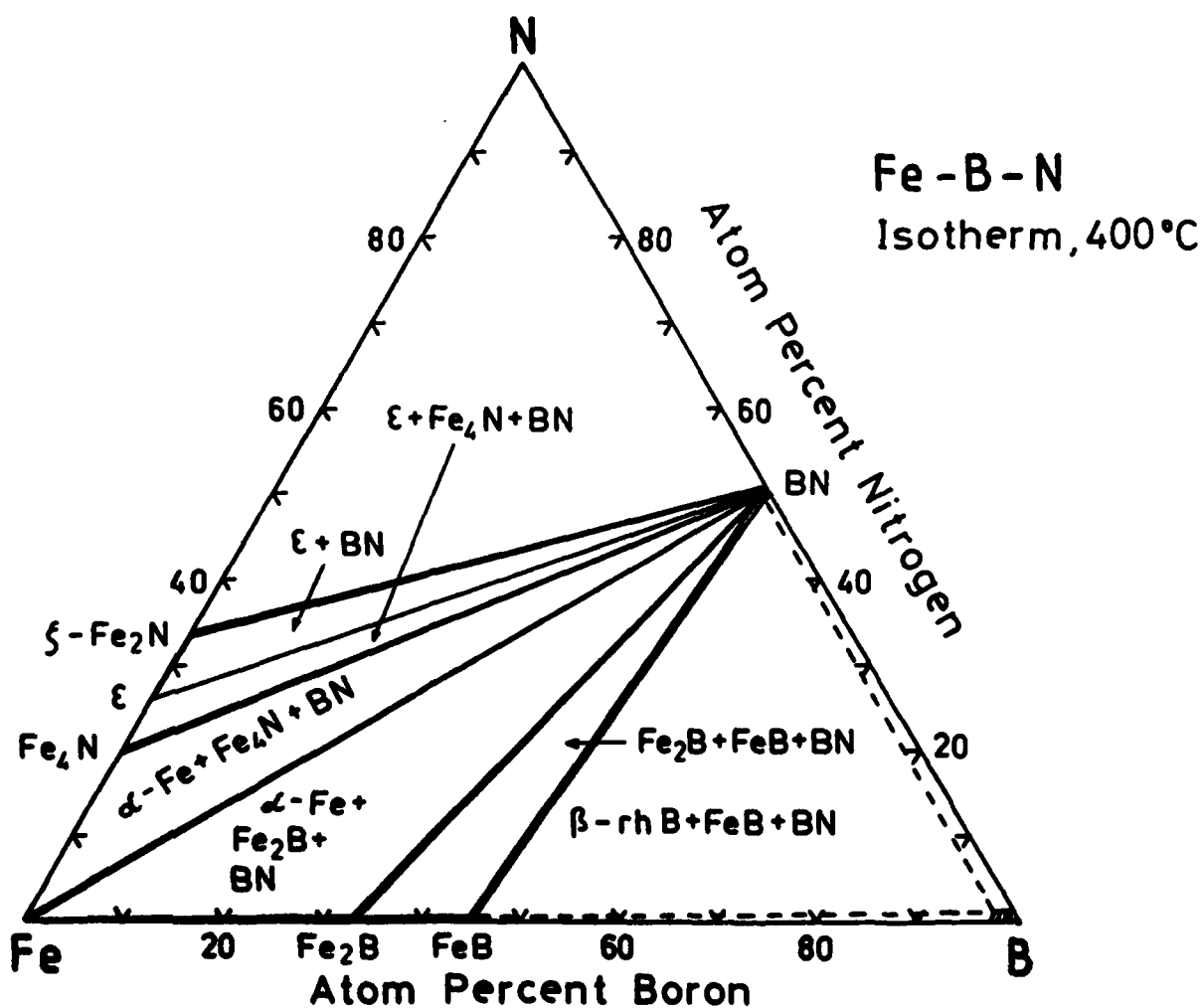


Fig.3 Phase equilibria in the iron rich corner of the system Fe - B - N at (a) 950°C, (b) 1050°C and (c) at 1150°C (after [62Fou], in mass percent).

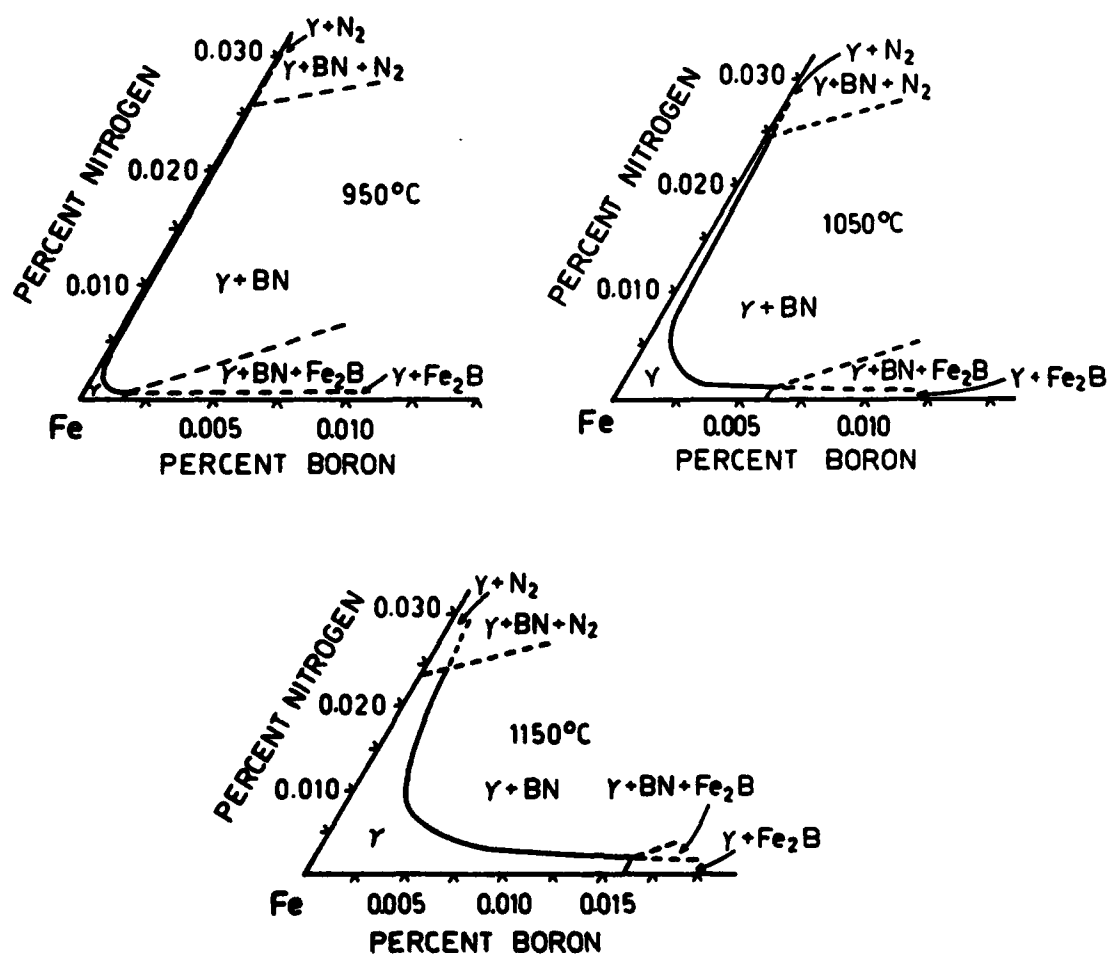


Fig.4 Isothermal section of the system B - Fe - N at 900°C under 1 bar of argon (in the absence of external nitrogen).

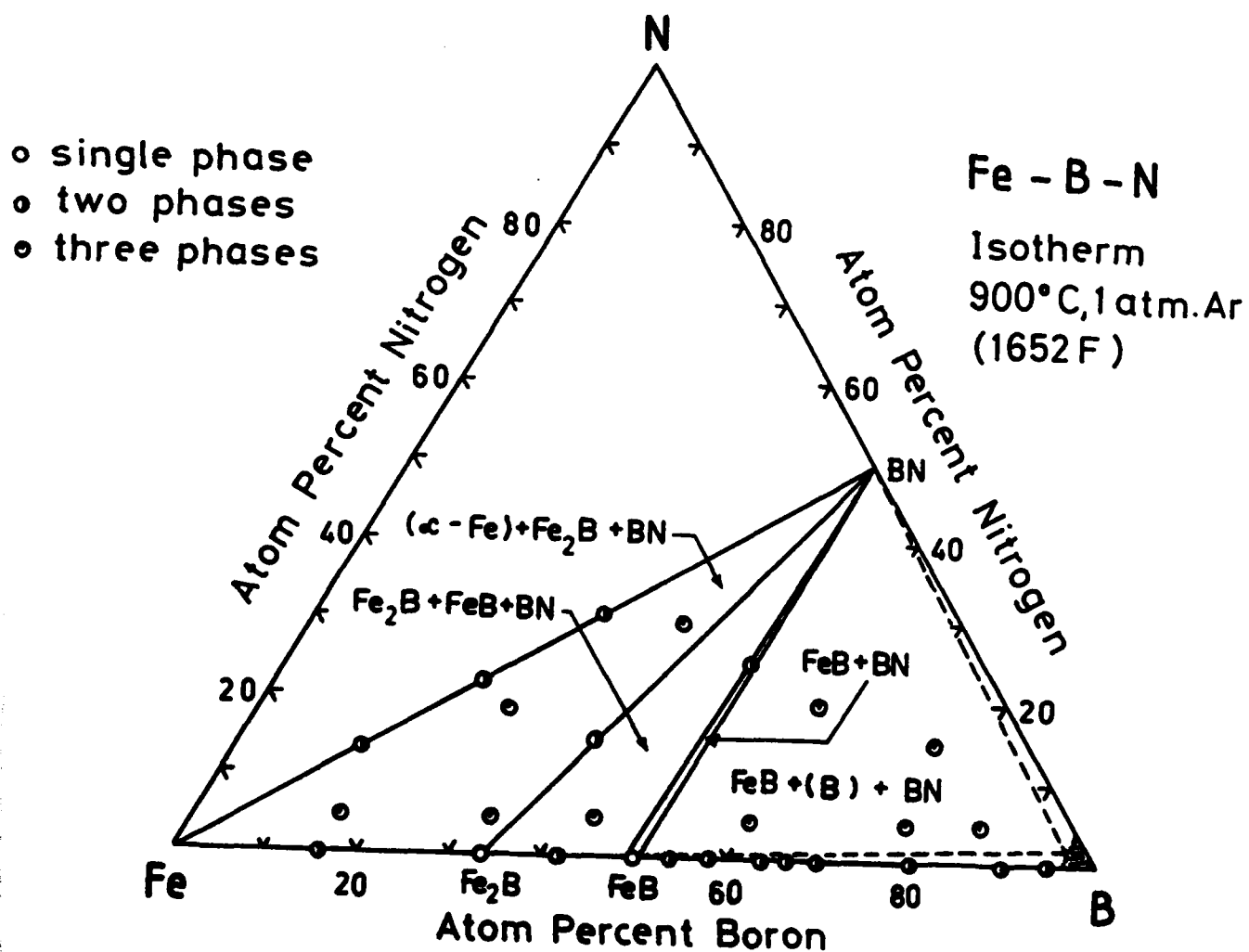
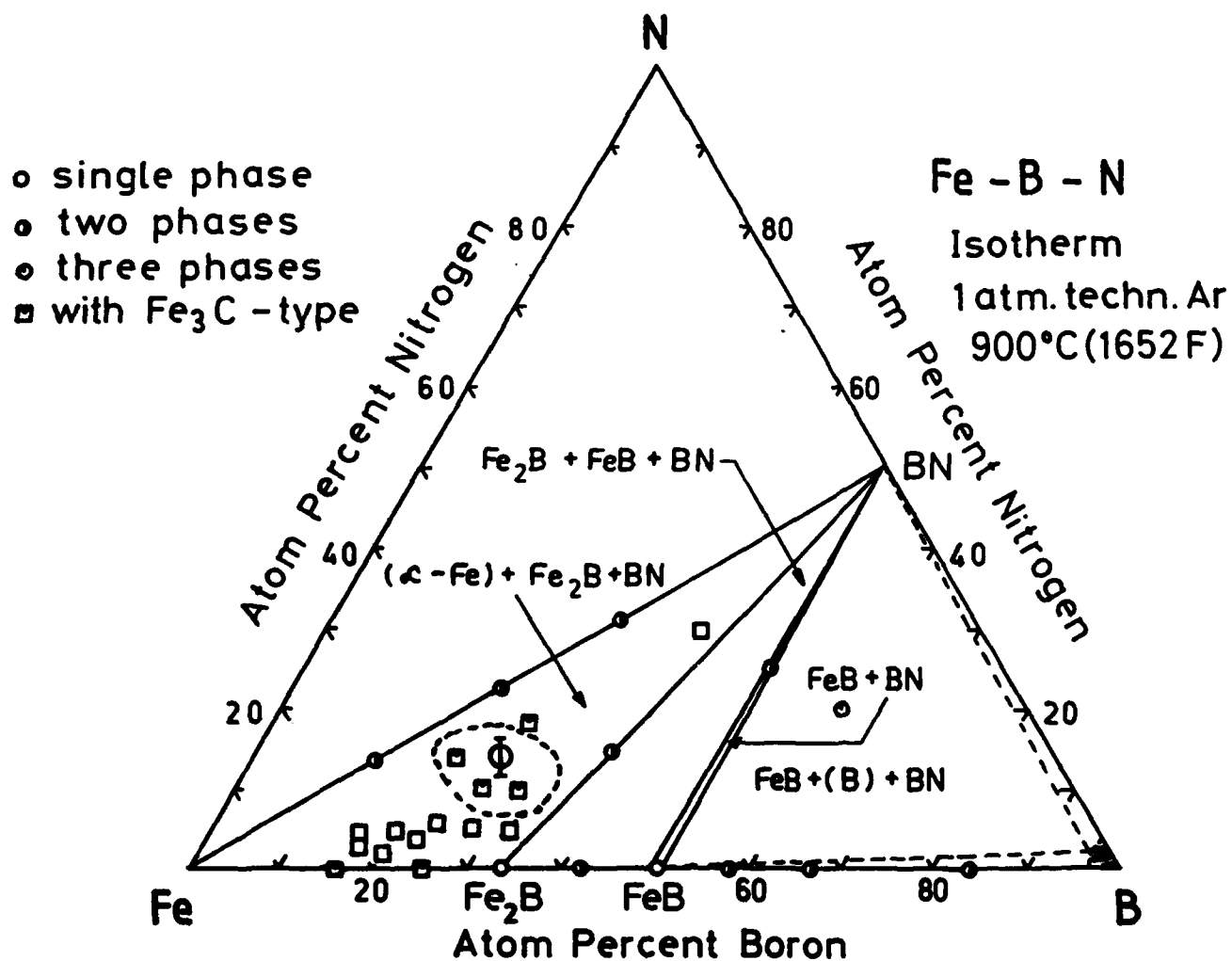


Fig.5 Isothermal section of the system Fe - B - N at 900°C under technical conditions ( 1 bar of technical argon, C-susceptor)



## SYSTEM BORON- COBALT- NITROGEN (B-Co-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Co-N system at 900°C have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, Co, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20 $\mu$ m in a steel mortar and/or a WC-Co mortar respectively [85<sup>V</sup>mi, 86<sup>V</sup>mi]. Annealing of the samples was either performed (a) in vacuum sealed silica tubes using a thin molybdenum foil to protect the sample from direct contact with the hot quartz wall or (b) in a 1 MHz-HF furnace under 1 bar of 6N-Ar or under various partial pressures of 6N-N<sub>2</sub> using hex-BN substrates in a tungsten or molybdenum susceptor crucible. Heat treatments usually consisted of a primary reaction at 900°C for 48h followed by a final reaction at 900°C up to 72h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were either monitored by calibrated microoptical pyrometry or by thermocouples; after heat treatment the samples were radiation cooled ( HF-furnace ) or quenched in water ( silica capsules ). The starting materials were powders from 3N-Co , crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements or by direct sintering under argon; weight losses were checked to be within 1 wt% [85<sup>V</sup>mi, 86<sup>V</sup>mi].

### BINARY SYSTEMS

The reinvestigation of the B-Co system at 900°C confirmed the existence of only three binary iron borides [86<sup>V</sup>mi], in essential consistency with the phase diagram as given in [90Mas, 88Lia]. The maximal solid solubility of boron in  $\alpha$ -Co was said to be 3 at% B at 1000°C [81Bas] and 5.2 at% B at 1100°C [38Koe]. From X-ray powder analysis the maximum solid solubility of Co in  $\beta$ -B was concluded to be about 3 to 5 at% Co at 1450°C [85<sup>V</sup>mid, 86<sup>V</sup>mi]; for crystallographic data see Table 1.

No phase diagram Co-N is available, however, the existence of a series of cobalt nitrides has been reported (see Table 1). All cobalt

nitrides easily decompose on heating at 276°C in vacuum and none is stable at 900°C at 10<sup>5</sup>Pa Ar [85<sup>V</sup>mi, 86<sup>V</sup>mi]. N was found to be practically insoluble in Co at p < 10<sup>5</sup>Pa N<sub>2</sub> and up to 1200°C [76Fro].

#### SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the phase relations in the Co-B-N system at 900°C [85<sup>V</sup>mi, 86<sup>V</sup>mi]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between cobalt and the binary cobalt-borides and BN. As seen from a comparison of the unit cell dimensions there is a small but significant solid solubility of Co in BN at 900°C, whereas mutual solubilities of the cobalt borides and BN are rather restricted [85<sup>V</sup>mi]. Alloys along the section Co-BN with a composition of about 20 mol % BN after heat treatment at 1350°C and 1 bar argon were reported to be molten and after quenching revealed the powder pattern of a cubic  $\tau$ -phase Co<sub>23</sub>(B,N)<sub>6</sub>.

The kinetic of nitriding was studied [86<sup>V</sup>mi] from binary cobalt boride samples annealed at 900 and 1250°C under 1 bar of 6N-nitrogen.

#### THERMODYNAMICS

A thermodynamic calculation/modelling of the binary system Co-B is due to [84Kau] and [88Lia]; see Table 2.

## REFERENCES

- [38Koe] W.Koester and U.W.Mulfinger, "The Binary Systems of Co with B,As,Zr,Nb and Ta", Z. fuer Metallkunde 30 (1938) 348-350
- [78Fro] E. Fromm, H. Jehn and G. Hoerz, "Gases and Carbon in Metals" ZAED, Physics Data,5-3 (1978) pp 2
- [81Bas] V.F.Bashev,I.S.Miroshnichenko and G.A.Sergeev,"New Metastable Phases of Cobalt-Boron, Iron-Boron and Nickel-Boron" (in Russian), Izv. Akad.Nauk SSSR, Neorg. Mater. 17(7) (1981) 1206-1211
- [84Kau] L.Kaufman, B.Uhrenius, D.Birnie and K.Taylor, "Coupled Pair Potential, Thermochemical and Phase Diagram Data For Transition Metal Binary Systems-VII",CALPHAD 8(1) (1984) 25-66
- [85Vil] P.Villars and L.D.Calvert,"Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park,Oh, 1985)
- [85Šmi] I.Šmid and P.Rogl, "Phase Equilibria and Structural Chemistry in Ternary Systems: Transition Metal - Boron Nitrogen", Proceedings of the 11<sup>th</sup> Int. Plansee Seminar (H.Bildstein and H.Ortner Eds.) Tyrolia, Innsbruck, Austria, Vol 2 (1985) 1029-1035
- [86Šmi] I.Šmid and P.Rogl, "Phase Equilibria and Structural Chemistry in Ternary Systems:Transition Metal-Boron-Nitrogen, Inst Phys.Conf.Ser.No.75: Chapter 4, Adam Hilger Ltd. (1986) 249-257
- [87Kii] O.Kiichi and Y.Tetsuo, J.Mater. Sci., 22 (1987) 2729
- [88Lia] P.K.Liao and K.E.Spear, "The B-Co System", Bull.Alloy Phase Diagrams 9 (1988) 452-457
- [90Mas] T.B.Massalski, "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., ASM, Metals Park, Ohio , (1990)

Table 1: Solid phases in the system B-Co-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\epsilon$ -Co(r) <422°	hP2 P6 <sub>3</sub> /mmc	a= 250.71 c= 406.86	[90Mas] at RT
$\alpha$ -Co(h) <1495°	cF4 Fm $\bar{3}$ m Cu	a= 354.47	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
		a=1094.59 c=2383.97	[85Vil] at CoB <sub>25</sub>
Co <sub>3</sub> B <1125°	oP16 Pbnm Fe <sub>3</sub> C	a= 440.8 b= 525.5 c= 662.9	[85Vil]
Co <sub>2</sub> B <1280°	tI12 I4/mcm Al <sub>2</sub> Cu	a= 501.6 c= 422.0	[85Vil]
CoB <1460°	oP8 Pbnm FeB	a= 395.6 b= 525.3 c= 304.3	[85Vil]
Co <sub>25</sub> B <sub>6</sub>	cF116 Fm $\bar{3}$ m Cr <sub>25</sub> C <sub>6</sub>	a=1106.	[85Vil] metastable
Co <sub>4</sub> N	cP5 Pm $\bar{3}$ m Fe <sub>4</sub> N	a= 358.6 a= 373.8	[87Kii] [85Vil]
Co <sub>3</sub> N	hP*	a= 274.6 c= 432.2	[85Vil]
Co <sub>2</sub> N	oP6 Pnnm Co <sub>2</sub> N	a= 460.56 b= 434.43 c= 285.35	[85Vil]

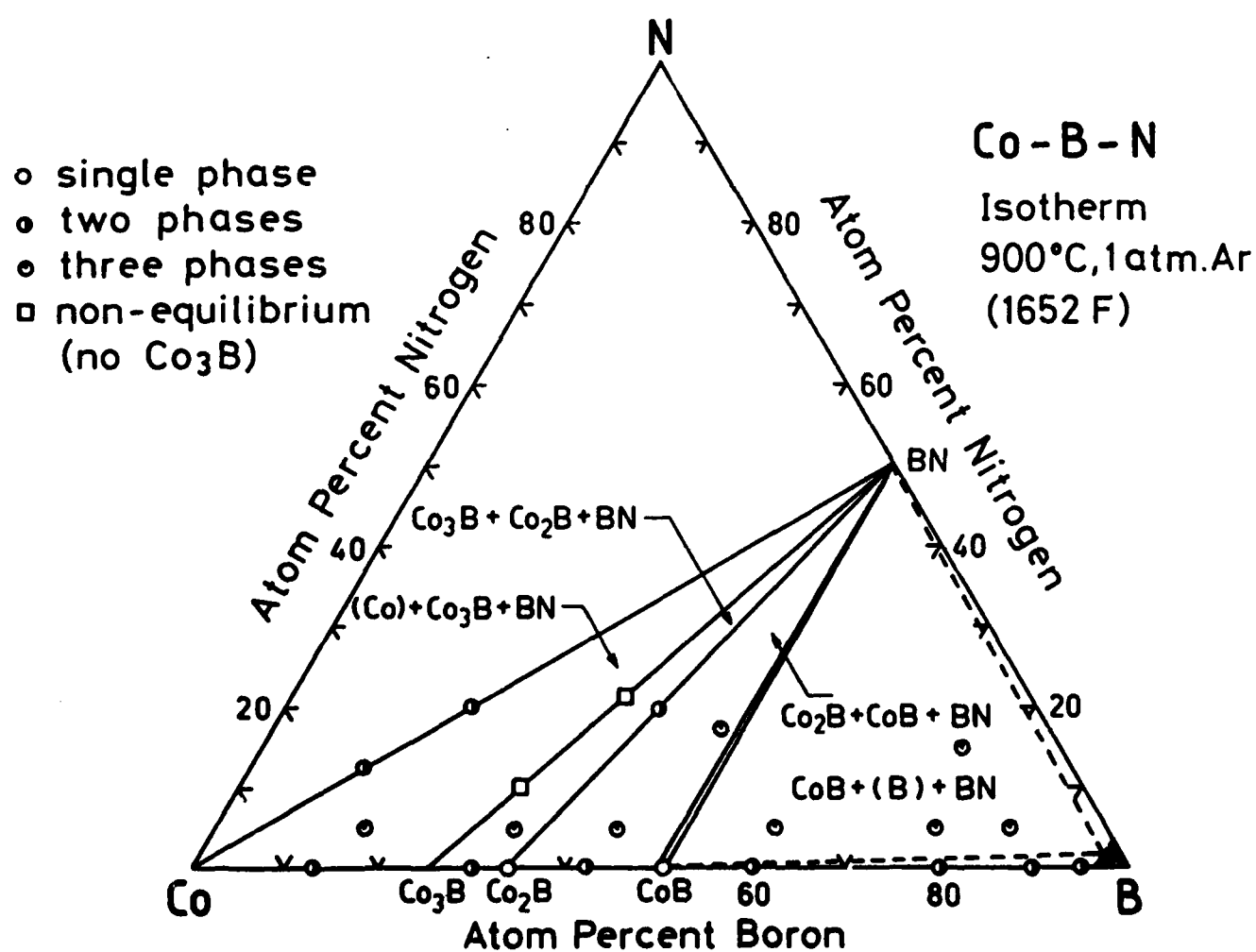


BN <sub>hex</sub>	hP5	a= 250.4	[85Vil]	
	P6 <sub>8</sub> /mmc	c= 868.1		
	BN <sub>hex</sub>			
* Co <sub>23</sub> (B,N) <sub>6</sub>	cF116	a=1048.3	[85 <sup>V</sup> ni]	metastable
	Fm $\bar{3}$ m			
	Cr <sub>23</sub> C <sub>6</sub>			

Table 2: Thermodynamic data for the system Co-B (after [88Lia])

Phase	$\Delta_f G$ ( J/granatom )	Ref.
1.0000 $\alpha$ Co	$\Delta_{fus} G(\text{Co}) = 16200 - 9.163 T$	[88Lia]
1.0000 B	$\Delta_{fus} G(\text{B}) = 50210 - 21.23 T$	
1.0000 Co	$\Delta_f G (\alpha\text{Co}) = 0$	
0.2500 Co <sub>3</sub> B	$\Delta_f G (\text{Co}_3\text{B}) = -25800 + 2.35 T$	
0.3333 Co <sub>2</sub> B	$\Delta_f G (\text{Co}_2\text{B}) = -26900 - 1.41 T$	
0.5000 CoB	$\Delta_f G (\text{CoB}) = -34500 + 0.24 T$	
1.0000 $\beta$ B	$\Delta_f G (\beta\text{B}) = 0$	
Liquid	$\Delta G^{ex} = x(1-x)\{-110700 - 7.46 T - 24500(1-2x) + 27100(1-2x)^2 + 21900(1-2x)^3\}$	

Fig.1 Isothermal section of the system B - Co - N at 900°C under 1 bar of argon (in the absence of external nitrogen).



## SYSTEM BORON- NICKEL- NITROGEN (B-Ni-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Ni-N system at 900°C have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, Ni, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than 20 $\mu$ m in a steel mortar and/or a WC-Co mortar respectively [85<sup>V</sup>mi, 86<sup>V</sup>mi]. Annealing of the samples was either performed (a) in vacuum sealed silica tubes using a thin molybdenum foil to protect the sample from direct contact with the hot quartz wall or (b) in a 1 MHz-HF furnace under 1 bar of 6N-Ar or under various partial pressures of 6N-N<sub>2</sub> using hex-BN substrates in a tungsten or molybdenum susceptor crucible. Heat treatments usually consisted of a primary reaction at 900°C for 72h followed by a final reaction at 900°C up to 72h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were either monitored by calibrated microoptical pyrometry or by thermocouples; after heat treatment the samples were radiation cooled ( HF-furnace ) or quenched in water ( silica capsules ). The starting materials were powders from 3N-Ni , crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C. Binary boride master alloys were prepared by arc melting the elements or by direct sintering under argon; weight losses were checked to be within 1 wt% [85<sup>V</sup>mi, 86<sup>V</sup>mi].

### BINARY SYSTEMS

The reinvestigation of the B-Ni system at 900°C confirmed the existence of five binary nickel borides [86<sup>V</sup>mi], in essential consistency with the phase diagram as given in [90Mas]. The maximal solid solubility of boron in Ni was said to be 0.3 at% B at 1085°C [65Sch]. From X-ray powder analysis the maximum solid solubility of Ni in  $\beta$ -B was concluded to be about 3 at% Ni at 1035°C [85<sup>V</sup>mid, 86<sup>V</sup>mi]; for crystallographic data see Table 1.

No phase diagram Ni-N is available, however, the existence of a series of nickel nitrides has been reported; for details see [76Fro] and [83Dor]. All nickel nitrides easily decompose on heating at 480°C

in vacuum and none is stable at 900°C at 10<sup>5</sup>Pa Ar [85<sup>Y</sup>mi, 86<sup>Y</sup>mi]. The solubility of N in Ni at 445 was said to amount to less than 0.3 at% N; the solubility of N in liquid Ni is rather small; for details see [76Fro].

#### SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the phase relations in the Ni-B-N system at 900°C [85<sup>Y</sup>mi, 86<sup>Y</sup>mi]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between nickel and the binary nickel-borides and BN. As seen from a comparison of the unit cell dimensions there is a small but significant solid solubility of Ni in BN at 900°C, whereas mutual solubilities of the nickel borides and BN are rather restricted [85<sup>Y</sup>mi]. Alloys along the section Ni-BN with a composition of about 20 mol % BN after heat treatment at 1350°C and 1 bar argon were reported to be molten and after quenching revealed the powder pattern of a cubic  $\tau$ -phase  $\text{Ni}_{23}(\text{B},\text{N})_6$ .

The kinetic of nitriding was studied [86<sup>Y</sup>mi] from binary nickel boride samples annealed at 900 and 1250°C under 1 bar of 6N-nitrogen.

#### THERMODYNAMICS

A thermodynamic modelling of the Ni-B system is due to [84Kau] and [81Hac].

## REFERENCES

- [85Sch] J.D.Schoebel and Stadelmaier, "The Binary System Ni-B",  
Z.fuer Metallkunde 56 (1985) 856-859
- [78Fro] E. Fromm, H. Jehn and G. Hoerz, "Gases and Carbon in Metals"  
ZAED, Physics Data, 5-3 (1978) pp 2
- [81Hac] K.Hack and T.Chart, "Estimation and Critical Assessment of  
Thermodynamic Data for the Cr-B, Mn-B, Fe-B and Ni-B Systems,  
NPL, England, private commun. (1981)
- [83Dor] G.J.W.R.Dorman and M.Sikkens, Thin solid Films 105 (1983) 251
- [84Kau] L.Kaufman, B.Uhrenius, D.Birnie and K.Taylor, " Coupled Pair  
Potential, Thermochemical and Phase Diagram Data for Transition  
Metal Binary Systems-VII", CALPHAD 8(1) (1984) 25-66
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of  
Crystallographic Data for Intermetallic Phases"  
(Amer.Soc.Met., Metals Park, Oh, 1985)
- [85Šmi] I.Šmid and P.Rogl, "Phase Equilibria and Structural  
Chemistry in Ternary Systems: Transition Metal - Boron  
Nitrogen", Proceedings of the 11<sup>th</sup> Int. Plansee  
Seminar (H.Bildstein and H.Ortner Eds.) Tyrolia, Innsbruck,  
Austria, Vol 2 (1985) 1029-1035
- [86Šmi] I.Šmid and P.Rogl, "Phase Equilibria and Structural Chemistry  
in Ternary Systems: Transition Metal-Boron-Nitrogen", Inst  
Phys.Conf.Ser.No.75: Chapter 4, Adam Hilger Ltd. (1986)  
249-257
- [90Mas] T.B.Massalski, "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed.,  
ASM, Metals Park, Ohio , (1990)

Table 1: Solid phases in the system B-Ni-N

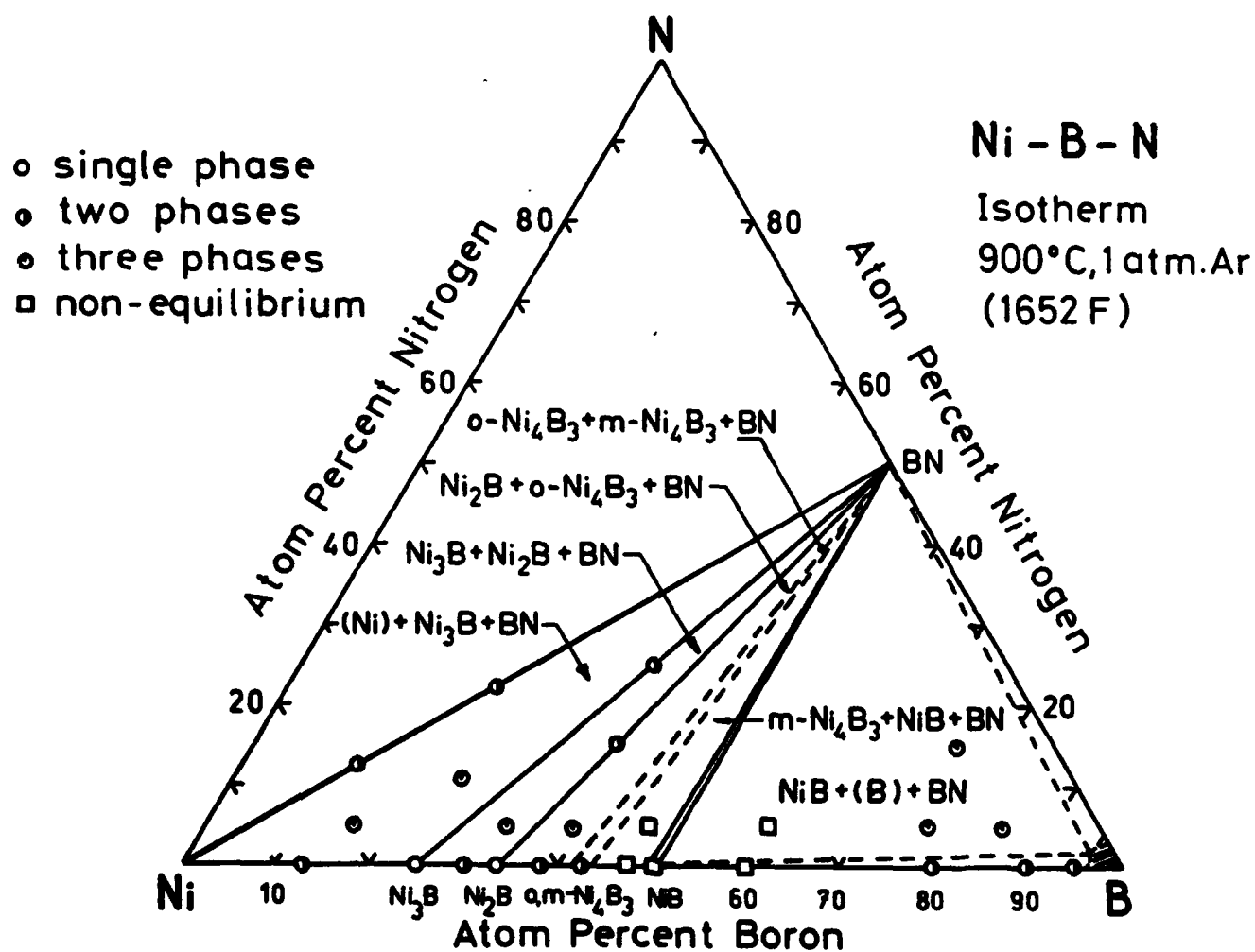
Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Ni <1455°	cF4 Fm $\bar{3}$ m Cu	a= 352.40	[90Mas] at RT
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43 a=1095.84 c=2385.46	[85Vil] [85Vil] [85Vil] at NiB <sub>20</sub>
Ni <sub>3</sub> B <1166°	oP16 Pbnm Fe <sub>3</sub> C	a= 439.0 b= 521.05 c= 661.74	[85Vil]
Ni <sub>2</sub> B <1125°	tI12 I4/mcm Al <sub>2</sub> Cu	a= 499.1 c= 424.7	[85Vil]
o-Ni <sub>4</sub> B <sub>3</sub> <1025°	oP28 Pnma o-Ni <sub>4</sub> B <sub>3</sub>	a=1195.40 b= 298.15 c= 656.84	[85Vil]
m-Ni <sub>4</sub> B <sub>3</sub> <1031°	mC28 C2/c m-Ni <sub>4</sub> B <sub>3</sub>	a= 842.82 b= 487.95 c= 781.90 $\beta$ =103.315°	[85Vil]
NiB <1035°	oP8 Cmcm CrB	a= 292.8 b= 739.1 c= 296.4	[85Vil]
Ni <sub>23</sub> B <sub>6</sub>	cF116 Fm $\bar{3}$ m Cr <sub>23</sub> C <sub>6</sub>	a=1048.	[85Vil] metastable
Ni <sub>4</sub> N	cP5 Pm $\bar{3}$ m Fe <sub>4</sub> N	a= 374.	[87Wri]

Ni <sub>3</sub> N	tP10	a= 372. c= 728.	[85Vil]	
Ni <sub>3</sub> N	hP*	a= 460.7	[85Vil]	
<400°, N <sub>2</sub>	P6 <sub>22</sub> or P312	c= 430.4		
BN <sub>hex</sub>	hP5	a= 250.4	[85Vil]	
	P6 <sub>22</sub> /mmc	c= 866.1		
	BN <sub>hex</sub>			
* Ni <sub>23</sub> (B,N) <sub>6</sub>	cF116 Fm $\bar{3}$ m Cr <sub>23</sub> C <sub>6</sub>	a=1044.8	[85 <sup>V</sup> ni]	metastable

Table 2: Thermodynamic data for the system Ni-B (after [81Hac])

Phase	$\Delta_f G$ ( J/granatom )	Ref.
1.0000 Ni	$\Delta_{fus} G(Ni) = 17479.82 - 10.1139 T$	[81Hac]
1.0000 B	$\Delta_{fus} G(B) = 50210 - 21.23 T$	
1.0000 Ni	$\Delta_f G(Ni) = 0$	
0.2500 Ni <sub>3</sub> B	$\Delta_f G(Ni_3B) = -22240 - 1.908 T$	
0.3333 Ni <sub>2</sub> B	$\Delta_f G(Ni_2B) = -21240 + 0.234 T$	
0.1465 Ni <sub>4</sub> B	$\Delta_f G(Ni_4B) = -25800 - 3.850 T$	
0.1410 Ni <sub>4</sub> B <sub>1-x</sub>	$\Delta_f G(Ni_4B_x) = -25850 - 4.179 T$	
0.5000 NiB	$\Delta_f G(NiB) = -23220 - 3.665 T$	
1.0000 $\beta B$	$\Delta_f G(\beta B) = 0$	
Liquid(Ni,B)	$\Delta G^{ex} = x(1-x)\{-150720 - 41.46 T + (-51080 - 8.50 T)(1-2x) + (54810 + 38.10 T)(1-2x)^2 + (41030 + 4.34 T)(1-2x)^3 + (-38280 - 25.68 T)(1-2x)^4\}$	

Fig.1 Isothermal section of the system B - Ni - N at 900°C under 1 bar of argon (in the absence of external nitrogen).





## SYSTEM BORON- RUTHENIUM- NITROGEN (B-Ru-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Ru-N system have been established from room temperature X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, Ru and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than  $20\mu\text{m}$  in a steel mortar and/or a WC-Co mortar respectively [88Rog]. For annealing the samples were kept on a hex-BN substrate within a molybdenum or tungsten susceptor crucible. Heat treatments in a 1 MHz-HF furnace ( under 1 bar of 5N-Ar or 5N-N<sub>2</sub> ) usually consisted of a primary reaction at  $1200^{\circ}\text{C}$  for 36h followed by a final reaction at  $1200^{\circ}\text{C}$  for 60h with an intermediate step of crushing and recompacting to ensure homogeneity. Temperatures were monitored by calibrated microoptical pyrometry and after heat treatment all samples were radiation cooled. Starting materials were powders of 3N-Ru, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at  $1400^{\circ}\text{C}$ . Binary boride master alloys were prepared by arc melting the elements together on a water cooled copper hearth [88Rog].

### BINARY SYSTEMS

The reinvestigation of the B-Ru system in the range from 800 to  $1400^{\circ}\text{C}$  revealed the existence of at least six binary ruthenium borides [88Rog]. Consistency with the data available in [84Vil] and [90Mas] is obtained for the formation and crystal structures of Ru<sub>7</sub>B<sub>8</sub>, Ru<sub>11</sub>B<sub>8</sub>, RuB, Ru<sub>2</sub>B<sub>3</sub>, and RuB<sub>2</sub>, whereas near the composition of Ru<sub>2</sub>B<sub>3</sub> two novel boride phases with a limited temperature region of existence were found labelled as Ru<sub>2</sub>B<sub>3-x</sub> and Ru<sub>2</sub>B<sub>3-y</sub>; see Table 1. Ru<sub>2</sub>B<sub>3-x</sub> was reported to decompose peritectoidally at temperatures above  $1275^{\circ}\text{C}$  and eutectoidally below ca  $1050^{\circ}\text{C}$  into RuB + Ru<sub>2</sub>B<sub>3</sub> [88Rog]. Due to the rather sluggish diffusion reactions in the high melting B-Ru system, thermodynamic equilibrium at  $1000^{\circ}\text{C}$  was not attained in those alloys which were arc melted prior to heat treatment at  $1000^{\circ}\text{C}$ .

Homogeneous ranges of the binary borides at  $1200^{\circ}\text{C}$  were found to

be rather small indicating a typical "line-compound" type of character.

The solid solubility of boron in ruthenium (interstitial type) was claimed to be less than 1.5 at%B at the temperature of the peritectic formation of  $\text{Ru}_7\text{B}_8$  (ca 1660°C) and was shown to rapidly decrease with decreasing temperature [63Obr]. From X-ray powder analysis the maximum solid solubility of Ru in  $\beta$ -B was concluded to be less than 0.5 at%Ru at 1800°C [81Cre].

Fig.1 represents the critically assessed version of the Ru-B phase diagram, temperature versus concentration.

No equilibrium diagram exists for the N-Ru system and solid solubility of N in Ru is said to be very small [78Fro].

#### SOLID PHASES / ISOTHERMAL SECTIONS

Figs.2,3 represent the isothermal sections at 1200°C and 1400°C respectively under 1 bar of argon (in the absence of external nitrogen pressure) [88Rog]. Phase equilibria are characterized by the absence of ternary compounds and by compatibility between the binary ruthenium-borides and BN. As seen from a comparison of the unit cell dimensions there is no significant solid solubility of Ru in BN at 1200°C and at 1400°C, and mutual solubilities of the ruthenium borides and BN are rather restricted [88Rog]. Whereas at 1200°C ruthenium metal is still compatible with BN, compatibility is lost at 1400°C owing to the reaction :  $7\text{Ru} + 3\text{BN} \rightleftharpoons \text{Ru}_7\text{B}_8 + 3/2\text{N}_2$ .

Phase equilibria in the Ru-B-N system have been also checked by nitriding the binary ruthenium boride powders under 1 bar of  $\text{N}_2$ . The results confirm the gradual decomposition of the higher borides via lower borides towards a limiting tie-line : (Ru) + BN. No signs of compound formation at higher nitrogen contents were observed.

## REFERENCES

- [63Obr] W.Obrowski, "On the Alloys of Ruthenium with Boron, Beryllium and Aluminium" (in German), Metall 17(2) (1963) 108-112
- [78Fro] E. Fromm, H. Jehn and G. Hoerz, "Gases and Carbon in Metals" ZAED, Physics Data, 5-3 (1978) pp 2
- [81Cre] A.J.Crespo, L.E.Tergenius and T.Lundstroem, "The Solid Solution of 4d, 5d and some p Elements in  $\beta$ rh Boron", J. Less-Common Metals, 77 (1981) 147-150
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallogr. Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, Oh, 1985)
- [88Rog] P.Rogl and C.Horvath "Phase Relations in The Ternary System :Ruthenium - Boron - Nitrogen", research at the Univ. Vienna, (1988), to be published
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met., Metals Park, Oh, 1990).

Table 1: Solid phases at 1200°C and 1400°C in the system B-Ru-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Ru <2334°	hP2 P6 <sub>3</sub> /mmc Mg	a= 270.58 c= 428.18	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
Ru <sub>7</sub> B <sub>3</sub> <1660°	hP20 P6 <sub>3</sub> mc Th <sub>7</sub> Fe <sub>3</sub>	a= 746.96 c= 471.55	[88Rog]
Ru <sub>11</sub> B <sub>8</sub> <1457°	oP38 Pbam Ru <sub>11</sub> B <sub>8</sub>	a=1161.58 b=1134.38 c= 283.61	[88Rog]
RuB <1520°	hP2 P $\bar{6}$ m2 WC (or def. AlB <sub>2</sub> )	a= 285.33 c= 285.57	[88Rog]
Ru <sub>2</sub> B <sub>3-y</sub> <1200°	unknown		[88Rog]
Ru <sub>2</sub> B <sub>3-x</sub> 1275-1025°	hP7	a= 500.42 c=1849.20	[88Rog]
Ru <sub>2</sub> B <sub>3</sub> <1800°	Ru <sub>2</sub> B <sub>3-x</sub> hP10 P6 <sub>3</sub> /mmm Ru <sub>2</sub> B <sub>3</sub>	a= 290.48 c=1280.94	[88Rog]
RuB <sub>2</sub> <1650°	oP6 Pmmn RuB <sub>2</sub>	a= 464.48 b= 286.56 c= 404.62	[88Rog]
BN <sub>hex</sub>	hP5 P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]

Fig.1: Assessed diagram of the binary system Ru - B

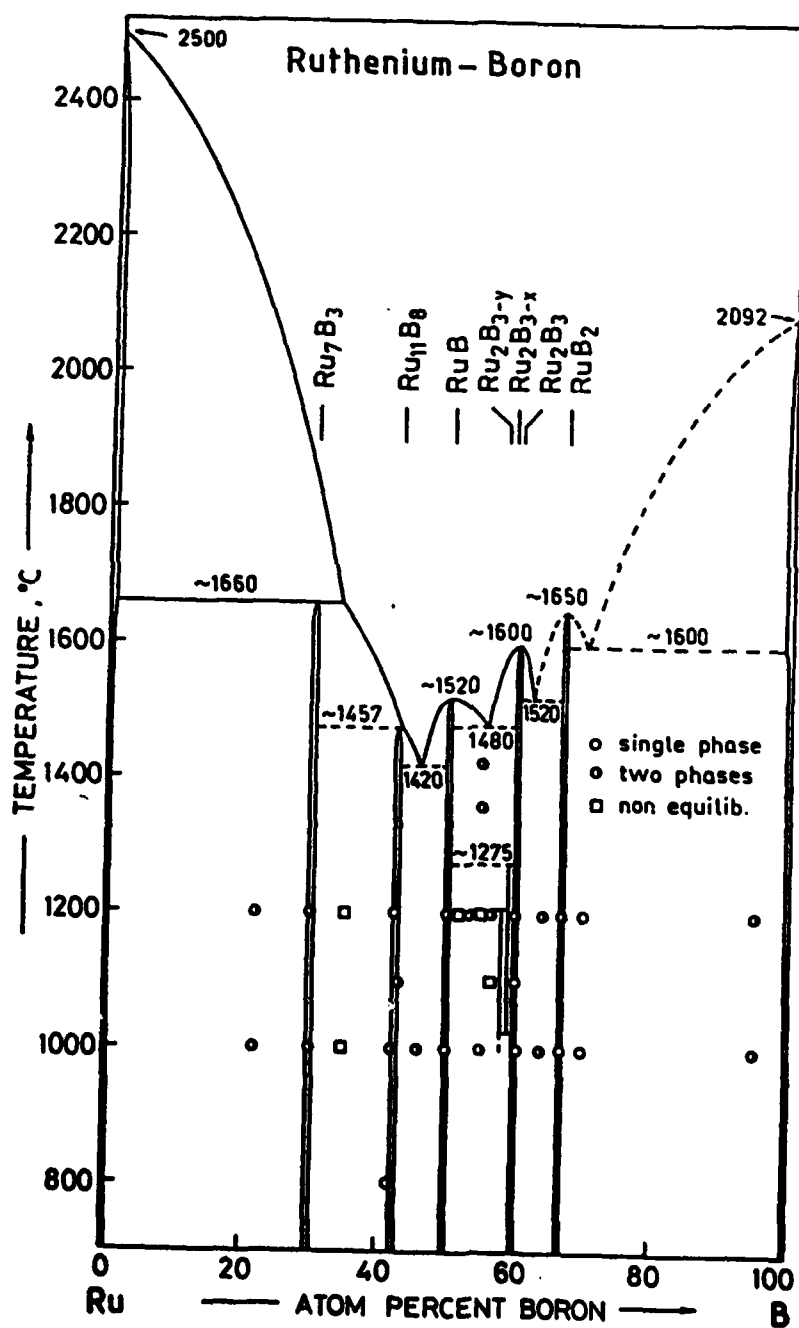


Fig.2: Isothermal section of the system B - Ru -N at 1200°C under 1 bar of argon ( in the absense of external nitrogen ).

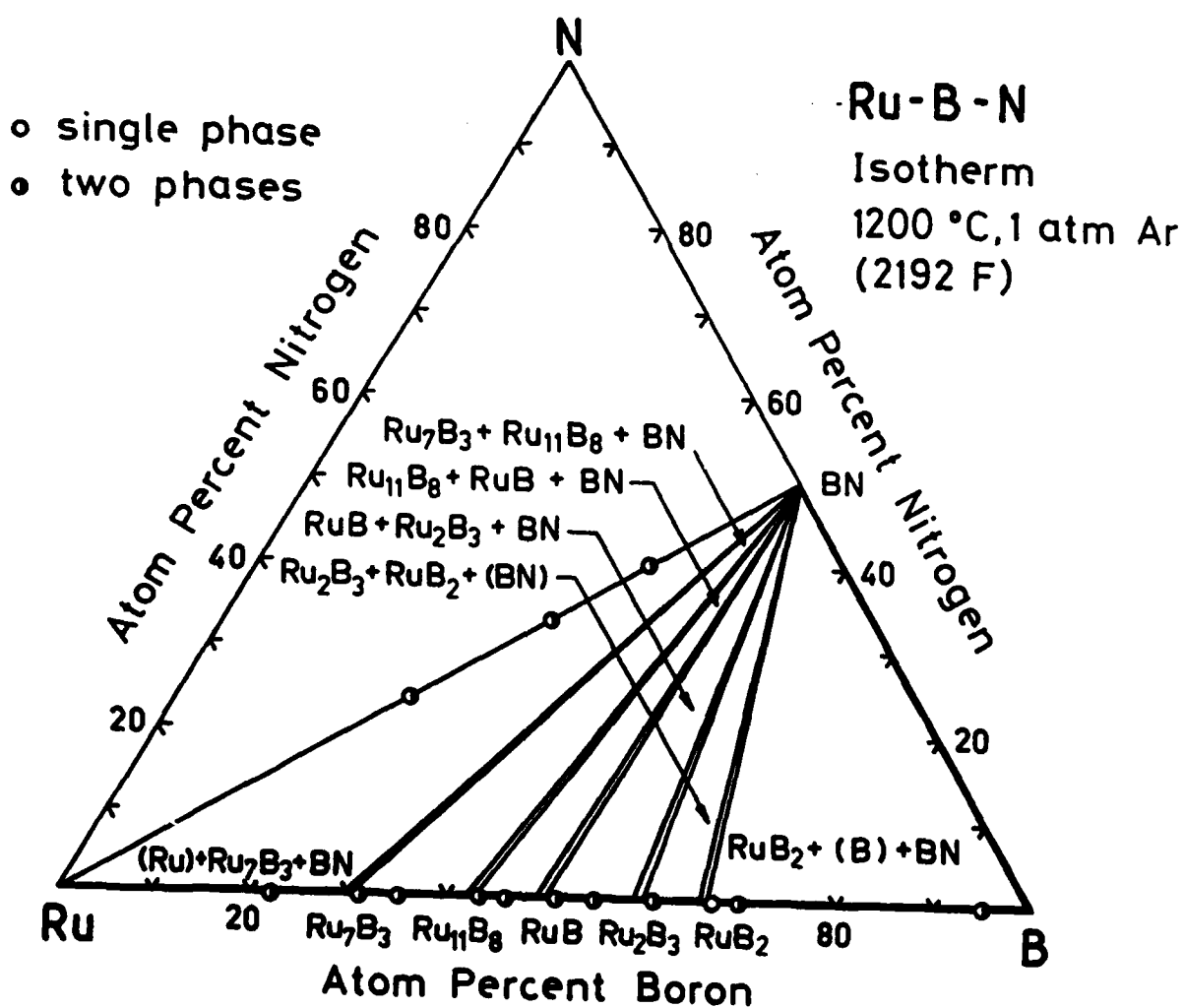
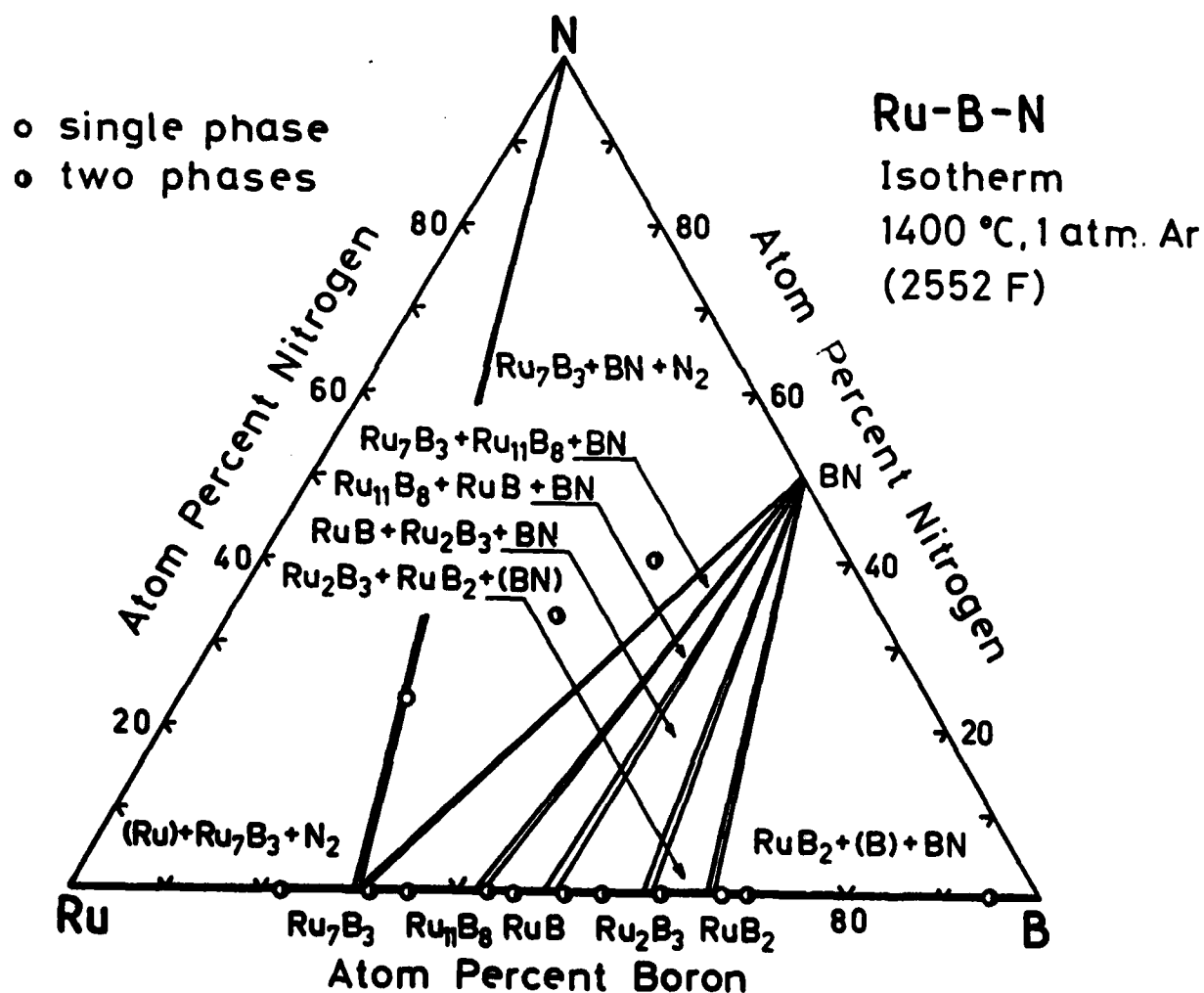


Fig.3 Isothermal section of the system B - Ru - N at 1400°C under 1 bar of argon (in the absence of external nitrogen ).



## SYSTEM BORON - COPPER - NITROGEN (B-Cu-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Cu-N system have been derived from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 900°C for a total of 800h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-Cu, crystallized boron (99.8 % B), hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C and GEC-cubic boron nitride of 99.8 % purity. After X-ray analysis the samples were exposed to 1 bar of nitrogen for an additional 400h at 900°C and examined.

### BINARY SYSTEMS

A tentative equilibrium diagram for the system B-Cu is represented in [90Mas]; for a detailed discussion see also [77Gur]. The equilibrium diagram is of a simple eutectic type ( $\sim 1013^{\circ}\text{C}$ ,  $\sim 13.3$  at%B) with a rather extended and retrograde solubility of Cu in  $\beta$ -rhombohedral boron [76Lun, 91Lun] ( $\sim 3$  at%Cu at  $1013^{\circ}\text{C}$ , 3.17 at%Cu at  $1300^{\circ}\text{C}$ , 3.47 at%Cu at  $1500^{\circ}\text{C}$  and 3.65 at%Cu at  $1700^{\circ}\text{C}$ ; see also Table 1). The solid solubility of B in Cu was said to be low ( $\sim 0.29$  at%Cu at  $1013^{\circ}\text{C}$  and 0.06 at%Cu at RT [86Mas]).

No phase diagram Cu-N is available yet, however, four binary compounds have been claimed to exist under various conditions:  $\text{Cu}_4\text{N}$ , prepared by d.c.-plasma ion nitriding of a Cu-sheet in a 260Pa -  $\text{N}_2/\text{H}_2$ - atmosphere at 450 to  $530^{\circ}\text{C}$ , probably is metastable [89Blu];  $\text{Cu}_3\text{N}$ , was reported to be stable in hydrogen up to ca  $310^{\circ}\text{C}$  [84Bai], whereas the azides  $\text{CuN}_3$  and  $\text{CuN}_5$  were synthesized at room temperature [48Wil, 88Soe]; Table 1. The solubility of nitrogen in copper is very low [76Pro].



## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 900°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Cu) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed in agreement with an earlier preliminary investigation of the reaction (l-Cu) + BN at 1100°C [65Yas].

## MISCELLANEOUS

The wetting angle of Cu on BN<sub>hex</sub>, as measured by the sessile drop method, was given as  $\Theta = 125^\circ$  [65Yas].

## REFERENCES

- [48Wil] H.Wilsdorf, "The Crystal Structure of the Monovalent Copper Azide Cu<sub>3</sub>N", Acta Crystallogr. 1 (1948) 115-118
- [65Yas] G.A.Yasinskaya, "Reactions of High Melting Compounds with Molten Metals" (in Russian), Ogneupory 30 (1965) 20-30
- [66Yas] G.A.Yasinskaya, "The Wetting of Refractory Carbides, Borides and Nitrides by Molten Metals", Sov. Powder Metall. and Metal Ceramics 7 (1966) 557-559, translated from Poroshkov. Met.(7) (1966) 53-56
- [68Soe] R.Soederqvist, "Studies on Explosives, I. The Crystal Structure of Copper(II)Azide, Catena-diazido copper (II)", Acta Crystallogr. 24B (1968) 450-455
- [74And] S.Andersson and B.Callmer, "The Solubilities of Cu and Mn in  $\beta$ -rh. Boron as Determined in CuB<sub>20</sub> and MnB<sub>20</sub> by Single Crystal Diffractometry", J.Solid State Chem.10 (1974) 219-31
- [76Lun] T.Lundstroem and L.E.Tergenius, "On the Solid Solution of Copper in  $\beta$ -rhombohedral Boron", J. Less Common Metals 47 (1976) 23-28
- [76Fro] E.Fromm and E.Gebhart, "Gases and Carbon in Metals" (in German) (Springer, Berlin, FRG, 1976)

- [76Hig] I.Higashi, T.Sakurai and T.Atoda, "Crystal Structure of  $\text{CuB}_{23}$ ", J.Less Common Metals 45 (1976) 283-292
- [77Gur] V.N.Gurin and M.M.Korsukova, "Ib and IIb Subgroup Borides " in "Boron and Refractory Borides " V.N. Matkovich (ed), (Springer, Berlin, Heidelberg, N.Y., 1977) 283-309
- [84Bai] A.Baiker and M.Maciejewski, "Formation and Thermal Stability of Copper and Nickel Nitrides", J.Chem.Soc.Faraday Trans.I 80 (1984) 2331-2341
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, Oh, 1985)
- [89Blu] J.Blucher, K.Bang and B.C.Giessen, "Preparation of the Metastable Interstitial Copper Nitride  $\text{Cu}_4\text{N}$  by d.c.-Plasma Ion Nitriding", Mater. Sci. Eng. A 117 (1989) L1-3
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M=Al, Cu, Zn, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi)", J.Mater.Res.5(10) (1990) 2152-2159
- [90Mas] T.B.Massalski (ed), "Binary Alloy Phase Diagrams" 2<sup>nd</sup> Ed., (Amer.Soc. Met.Intl., Metals Park, Oh, 1990)
- [91Lun] T.Lundstroem, "Solid Solutions Of Transition and Inner Transition Metals in Boron", in Inorganic Reactions and Methods", J.J.Zuckerman ( ed ) (Verlag Chemie, Weinheim, 1991)

Table 1: Solid phases at 900°C in the system B - Cu - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Cu <1084.9°	cF4 Fm $\bar{3}$ m Cu	a= 361.49	[86Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1093.02 c=2381.66	[76Lun]
		a=1093.32 c=2382.92	[76Lun] for CuB <sub>443.9</sub>
		a=1093.77 c=2384.27	[76Lun] for CuB <sub>170.6</sub>
		a=1094.38 c=2386.28	[76Lun] for CuB <sub>86.7</sub>
		a=1096.05 c=2387.93	[76Lun] for CuB <sub>42.2</sub>
		a=1097.23 c=2388.94	[74And] for CuB <sub>28</sub>
		a=1098.5 c=2392.5	[76Hig] for CuB <sub>28</sub>
Cu <sub>4</sub> N	cP5 Pn $\bar{3}$ m or P $\bar{4}$ 3m Fe <sub>4</sub> N	a= 319.3	[85Vil] metastable
Cu <sub>8</sub> N	cP4 Pn $\bar{3}$ m ReO <sub>8</sub>	a= 381.3	[85Vil]
CuN <sub>8</sub>	tI32 I4 <sub>1</sub> /a	a= 865.3 c= 559.4	[85Vil]
CuN <sub>6</sub>	cP28 Pnma	a=1348.1 b= 308.4 c= 907.6	[85Vil]

$BN_{hex}$

$hP^*$

$a = 250.4$

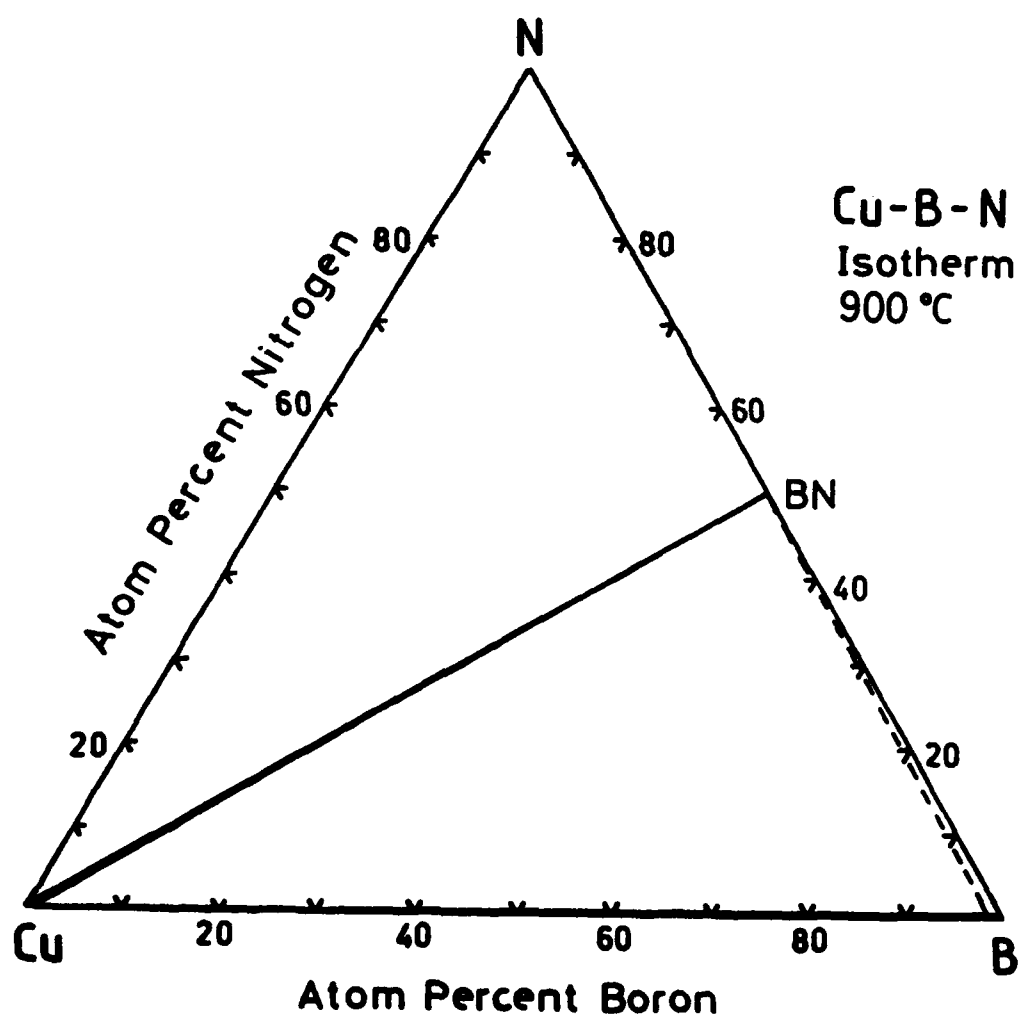
[85V11]

$P6_g/nmc$

$c = 666.1$

$BN_{hex}$

Fig 1: Isothermal section at 900°C in the system B - Cu - N



## SYSTEM BORON - SILVER - NITROGEN (B-Ag-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Ag-N system have been derived from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 800°C for a total of 700h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of silver (Ögussa, "puriss"), crystallized boron (99.8 % B), hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C, and GEC-cubic boron nitride of 99.8 % purity. After X-ray analysis the samples were exposed to 1 bar of nitrogen for an additional 400h at 800°C and examined.

### BINARY SYSTEMS

A tentative equilibrium diagram for the system B-Ag which is supposed to be of a simple monotectic type with negligible solid solubility of B in Ag and without the existence of equilibrium compounds is presented in [Mof]; a detailed discussion is found in [77Gur]. The compound "AgB<sub>2</sub>", claimed to crystallize with the AlB<sub>2</sub>-type (C32, hP3 - P6/mmm, a=300.0, c= 324.0pm [61Obr]), is likely to be metastable, and has not been confirmed yet. A small solid solubility of Ag in  $\beta$ -rhombohedral boron is inferred from the X-ray data on an arc melted alloy [81Cre]; see Table 1.

No phase diagram exists for the system Ag-N, however, the existence of two compounds, which are unstable above 300°C, has been reported: Ag<sub>3</sub>N and AgN<sub>3</sub> (see Table 1). The solubility of N in silver is very small [76Fro]. A critical assessment of the data available on the Ag-N system is due to [90Kar].

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 800°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Ag) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed [90Wei].

## REFERENCES

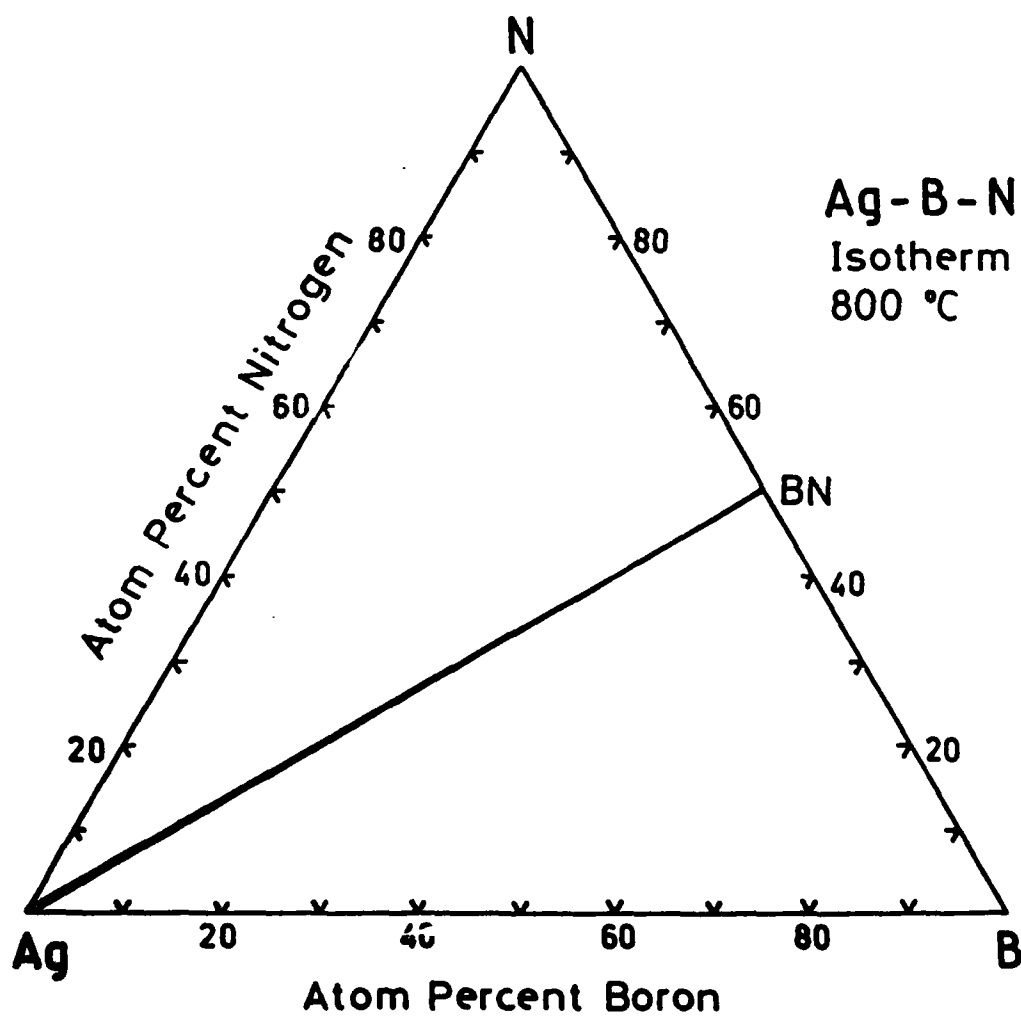
- [81Obr] W.Obrowski, "The Crystal Structure of The Diborides of Gold and Silver " (in German), Naturwiss. 48 (1961) 428
- [76Fro] E.Fromm and E Gebhardt, "Gases and Carbon in Metals" (in German) (Springer,Berlin,FRG, 1978)
- [77Gur] V.N.Gurin and M.M.Korsukova,"Ib and IIb Subgroup Borides " in "Boron and Refractory Borides ", V.N. Matkovich (ed), (Springer,Berlin,Heidelberg,N.Y.,1977) 293-309
- [81Cre] A.J.Crespo,L.E.Tergenius and T.Lundstroem, "The Solid Solution of 4d, 5d, and Some p-Elements in  $\beta$ -rhombohedral Boron", J.Less Common Metals 77 (1981) 147-150
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer. Soc. Met. ,Metals Park, Oh, 1985)
- [90Wei] F.Weitzer, K.Renschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M=Al,Cu,Zn,Ag,Cd,In,Sn,Sb,Au,Tl,Pb,Bi)" J.Mater.Res. 5 (1990) 2152-2159
- [90Kar] I.Karakaya and W.T.Thompson, "The Ag-N System", Bull.Alloy Phase Diagrams 11 (1990) 486-487
- [90Mas] T.B.Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met.,Metals Park,Oh, 1990)

Table 1: Solid phases at 800°C in the system B - Ag - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Ag <961.93°	cF4 Fm $\bar{3}$ m Cu	a= 408.61	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.65 c=2380.96  a=1093.55 c=2384.40	[81Cre]  [81Cre] for AgB <sub>x</sub>
Ag <sub>3</sub> N	cF*	a= 437.8	[85Vil]
AgN <sub>8</sub>	oI16 Iban KN <sub>8</sub> -deriv.	a= 561.70 b= 591.46 c= 600.57	[85Vil]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]



Fig.1: Isothermal section at 800°C in the system B - Ag - N



## SYSTEM BORON - GOLD - NITROGEN (B-Au-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Au-N system have been derived from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 800°C for a total of 1400h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-Au, crystallized boron (99.8 % B), hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C and GEC-cubic boron nitride of 99.8 % purity. After X-ray analysis the samples were exposed to 1 bar of nitrogen for an additional 400h at 800°C and examined.

### BINARY SYSTEMS

A tentative equilibrium diagram for the system Au-B is shown in [90Mas]; a detailed discussion is also presented by [77Gur]. Without the existence of equilibrium compounds, the system Au-B is suggested to be of a simple monotectic type with negligible solid solubilities of Au, B. For the solubility of Au in  $\beta$ -B see [81Cre] and Table 1. The compound "AuB<sub>2</sub>", claimed to crystallize with the AlB<sub>2</sub>-type (C32, hP3 - P6/mmm, a=314, c= 352pm [61Obr] ), is likely to be metastable, and has not been confirmed yet.

No phase diagram exists for the system Au-N, however, a critical assessment of the existing information is available by [84Oka]; the formation of two probably metastable compounds Au<sub>3</sub>N<sub>2</sub> and AuN<sub>3</sub> both with unknown crystal structure is mentioned [84Oka]. The solubility of N in Au is negligible [84Oka,78Pro].

### SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 800°C in the absence of external nitrogen pressure. Phase equilibria are characterized by compatibility of (Au) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed.

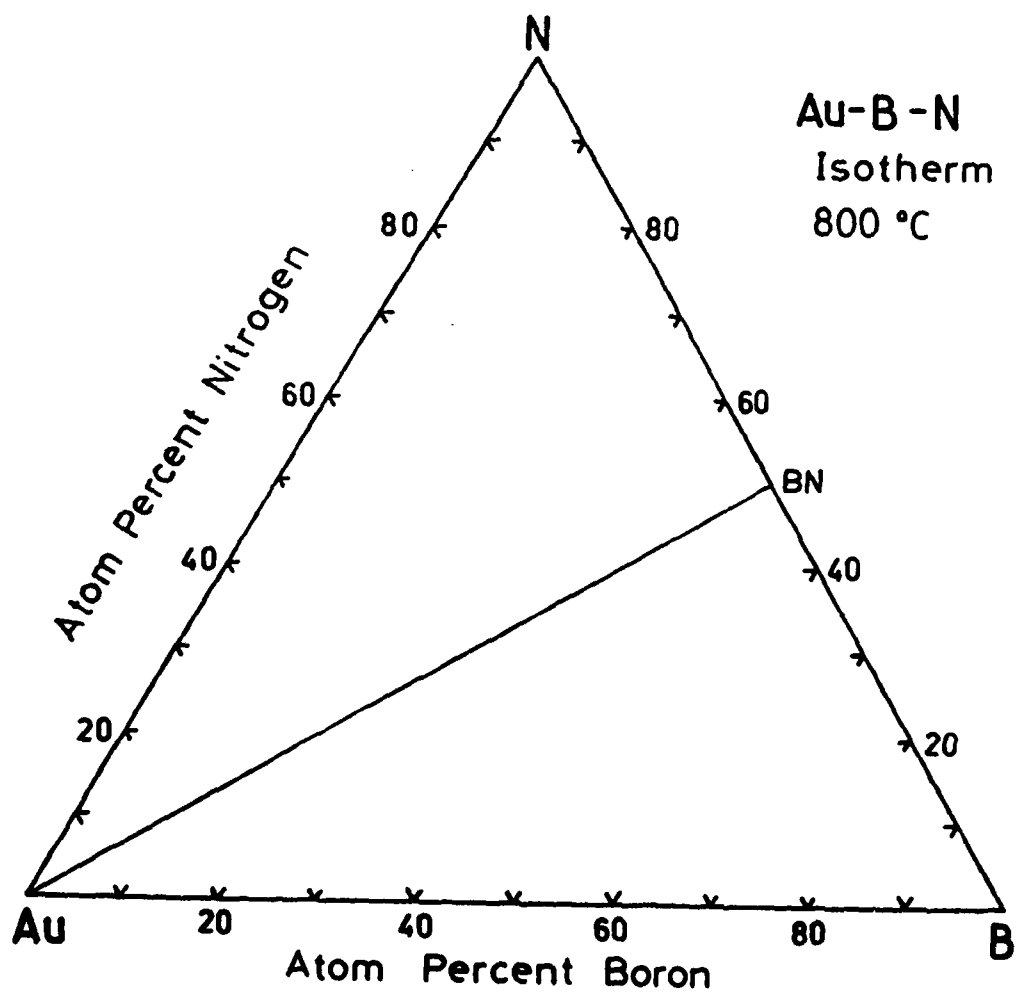
## REFERENCES

- [61Obr] W.Obrowski, "The Crystal Structure of the Diborides of Gold and Silver " (in German), Naturwiss. 48 (1961) 428
- [76Fro] E.Fromm and E.Gebhardt, " Gases and Carbon in Metals " (in German) (Springer,Berlin,FRG, 1976)
- [77Gur] V.N.Gurin and M.M.Korsukova,"Ib and IIb Subgroup Borides",in "Boron and Refractory Borides " V.N. Matkovich (ed), (Springer,Berlin,Heidelberg,N.Y.,1977) 293-309
- [81Cre] A.J.Crespo, L.E.Tergenius and T.Lundström, "The Solid Solution of 4d, 5d, and Some p-Elements in  $\beta$ -rhombohedral Boron", J.Less Common Metals 77 (1981) 147-150
- [84Oka] H.Okamoto and T.B.Massalski, "The Au - N (Gold - Nitrogen) System", Bull. Alloy Phase Diagrams 5 (1984) 381-382
- [85Vil] P.Villars and L.D.Calvert, " Pearsons Handbook of Crystallographic Data for Intermetallic Phases (Amer.Soc.Met.,Metals Park,Oh, 1985)
- [90Mas] T.B.Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met.,Metals Park,Oh, 1990)
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M=Al,Cu,Zn,Ag,Cd,In,Sn,Sb,Au,Tl,Pb,Bi)" J.Mater.Res. 5 (1990) 2152-2159

Table 1: Solid phases at 800°C in the system B - Au - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Au <1064.4°	cF4 Fm $\bar{3}$ m Cu	a= 407.84	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil]
		a=1093.24 c=2382.38	[81Cre] for AuB <sub>x</sub>
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section at 800°C in the system B - Au - N



## SYSTEM BORON - ZINC - NITROGEN (B-Zn-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Zn-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 375°C for a total of 850h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-Zn, crystallized boron (99.8 % B), hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C.

### BINARY SYSTEMS

A tentative equilibrium diagram for the system B-Zn is given in [Mof], however, does not account for the observed solid solubility of Zn in boron (see below); a comprehensive discussion of all reported information has been given by [77Gur]. There is no binary boride known and there is practically no solubility of B in Zn, whereas a rather extended solid solution  $B_{100-x}Zn_x$  ( $x < 5$ ) exists in  $\beta$ -rh boron ( $\sim B_{22}Zn$ , [87Kuz]) as well as in  $\alpha$ -rh boron ( $< 1.3$  at% Zn, [77Kor]); see Table 1. The interaction of Zn with the various modifications of boron at 500 to 900°C has been studied by [77Kor].

According to a recent critical assessment of the system N-Zn [88Wri] two binary compounds are known to exist:  $Zn_8N_2$  (see Table 1), which was claimed to be stable up to 550°C under  $N_2$ , but decomposes in vacuum above 350°C [88Wri] and  $ZnN_6$ , which decomposes on heating around 300°C and for which two structural modifications have been reported (see Table 1) [88Wri]. Interstitial solubility of N in Zn is very low [88Wri].

### SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 375°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Zn) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary

compounds have been observed in agreement with an earlier preliminary investigation of the reaction  $(\text{l-Zn}) + \text{BN}$  at  $940^\circ\text{C}$  [65Yas].

## REFERENCES

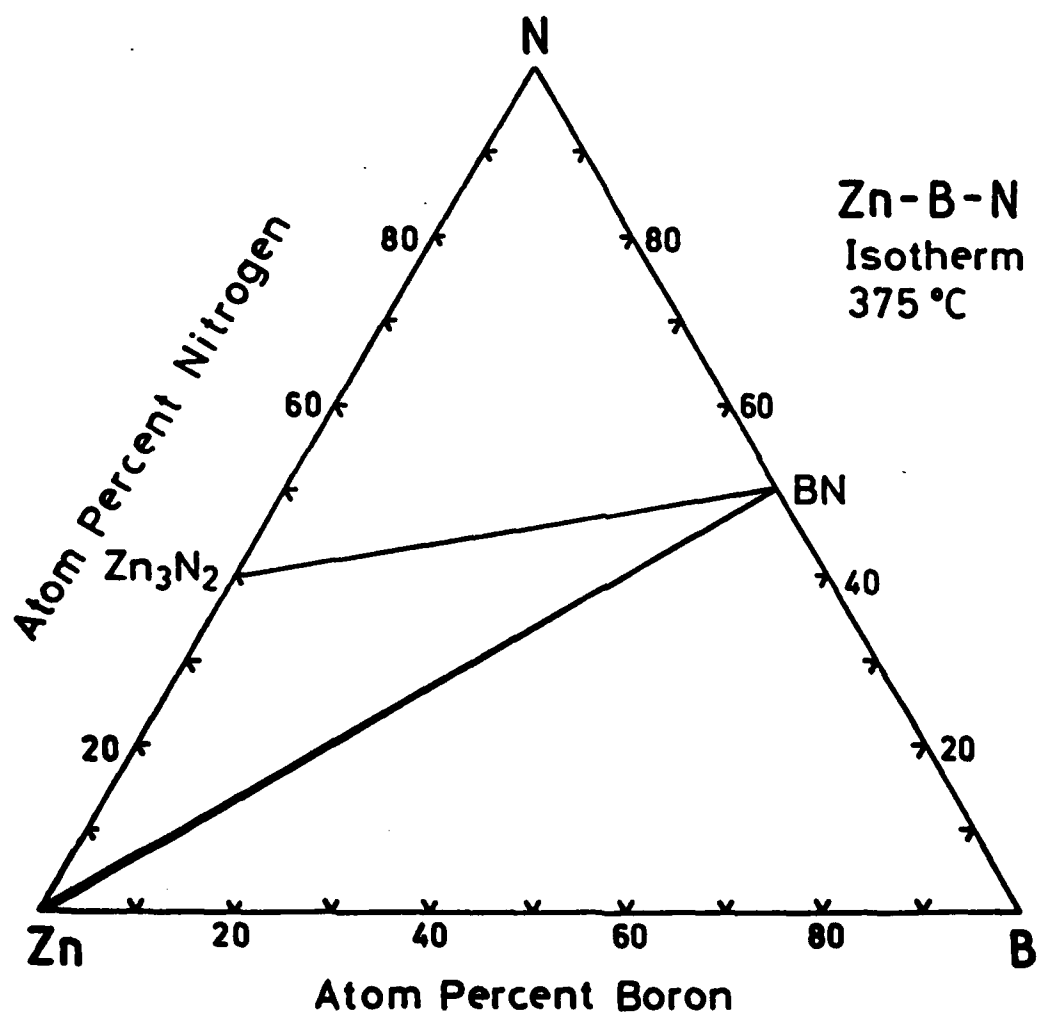
- [65Yas] G.A.Yasinskaya, "Reactions of High Melting Compounds with Molten Metals" , *Ogneupory* 30 (1965) 20-30
- [77Gur] V.N.Gurin and M.M.Korsukova, " Ib and IIb Subgroup Borides " in "Boron and Refractory Borides", V.N.Matkovich (ed), (Springer,Berlin,Heidelberg,N.Y.,1977) 293-309
- [77Kor] M.M.Korsukova, V.N. Gurin, Yu.B.Kuz'ma, A.Yu.Kiskachi and N.E.Solov'ev, "Structural Changes induced in Various Modifications of Boron by Zinc", *Sov.Phys.Crystallogr.* 22 (1977) 690-692, translated from *Kristallografija* 22 (1977) 1214-1218
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc. Met., Metals Park,Oh, 1985)
- [87Kuz] Yu.B.Kuz'ma, V.I.Gurin, M.M.Korsukova and L.G.Akselrud, "Crystal Structure of the Phase  $\text{ZnB}_{25}$ " (in Russian), *Izv.Akad. Nauk SSSR, Neorg. Mater.* 23 (1987) 566-570
- [88Wri] H.A.Wriedt, "The N-Zn (Nitrogen-Zinc) System" , *Bull. Alloy Phase Diagrams* 9 (1988) 247-251
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M=Al,Cu,Zn,Ag,Cd,In,Sn,Sb,Au,Tl,Pb,Bi)", *J.Mater.Res.* 5 (1990) 2152-2159
- [90Mas] T.B.Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met., Metals Park,Oh, 1990)

Table 1: Solid phases at 375°C in the system B-Zn-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Zn <418.6°	hP2 P6 <sub>3</sub> /mmc Mg	a= 266.44 c= 494.94	[90Mas]
β-rhB <2092°	hR111 R $\bar{3}$ m β-B	a=1092.51 c=2381.43	[85Vil] [85Vil]
		a=1098.6 c=2401.6	[87Kuz] for ZnB <sub>25</sub>
		a=1093 c=2374	[77Kor]
		a=1101 c=2317	[77Kor] for ZnB <sub>210</sub>
		a=1100 c=2404	[77Kor] for ZnB <sub>29</sub>
α-rhB <1200°	hR36 R $\bar{3}$ m α-B	a= 490.9 c= 1258.2	[77Kor]
		a= 491.0 c=1258.2	[77Kor] for ZnB <sub>80</sub>
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 886.1	[85Vil]
Zn <sub>9</sub> N <sub>2</sub>	cI80 Ia $\bar{3}$ Mn <sub>2</sub> O <sub>9</sub>	a= 976.3	[85Vil]
α-ZnN <sub>6</sub>	oP36 P222 <sub>1</sub>	a=1098 b= 692 c=1633	[85Vil] [88Wri] gives Pcmn-oP84
β-ZnN <sub>6</sub>	o*28	a= 735 b= 437 c=1523	[88Wri]



Fig.1: Isothermal section at 375°C in the system B - Zn - N



## SYSTEM BORON - CADMIUM - NITROGEN (B-Cd-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Cd-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 250°C for a total of 350h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-Cd, crystallized boron (99.8 % B), hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C and GEC-cubic boron nitride of 99.8 % purity.

### BINARY SYSTEMS

A tentative equilibrium diagram for the system B-Cd is given in [Mof]. A binary compound "CdB<sub>6</sub>" has been mentioned earlier but is supposed to be metastable or ill characterized; for a more detailed discussion see [77Gur]. B was said to be insoluble in Cd and whereas the solubility of Cd in  $\beta$ -B is said to be very low, ~5 mass% Cd was reported to dissolve in  $\alpha$ -B at 800°C [77Gur].

According to a recent critical assessment of the system Cd-N [88Wri], the formation of two binary compounds has been reported: Cd<sub>3</sub>N<sub>2</sub> and CdN<sub>6</sub>; see Table 1. Whereas Cd<sub>3</sub>N<sub>2</sub> was reported to decompose slowly at 180°C in an atmosphere of NH<sub>3</sub> (pressure not specified, [88Wri]), the azide CdN<sub>6</sub> decomposes nonexplosively when heated slightly above 100°C [88Wri]. The solubility of N in Cd is small [88Wri].

### SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 250°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Cd) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed in agreement with an earlier preliminary investigation of the reaction (l-Cd) + BN at 550°C [85Yas].

## MISCELLANEOUS

Nonwetting behavior ( $\theta > 90^\circ$ ) was claimed by [85Yas].

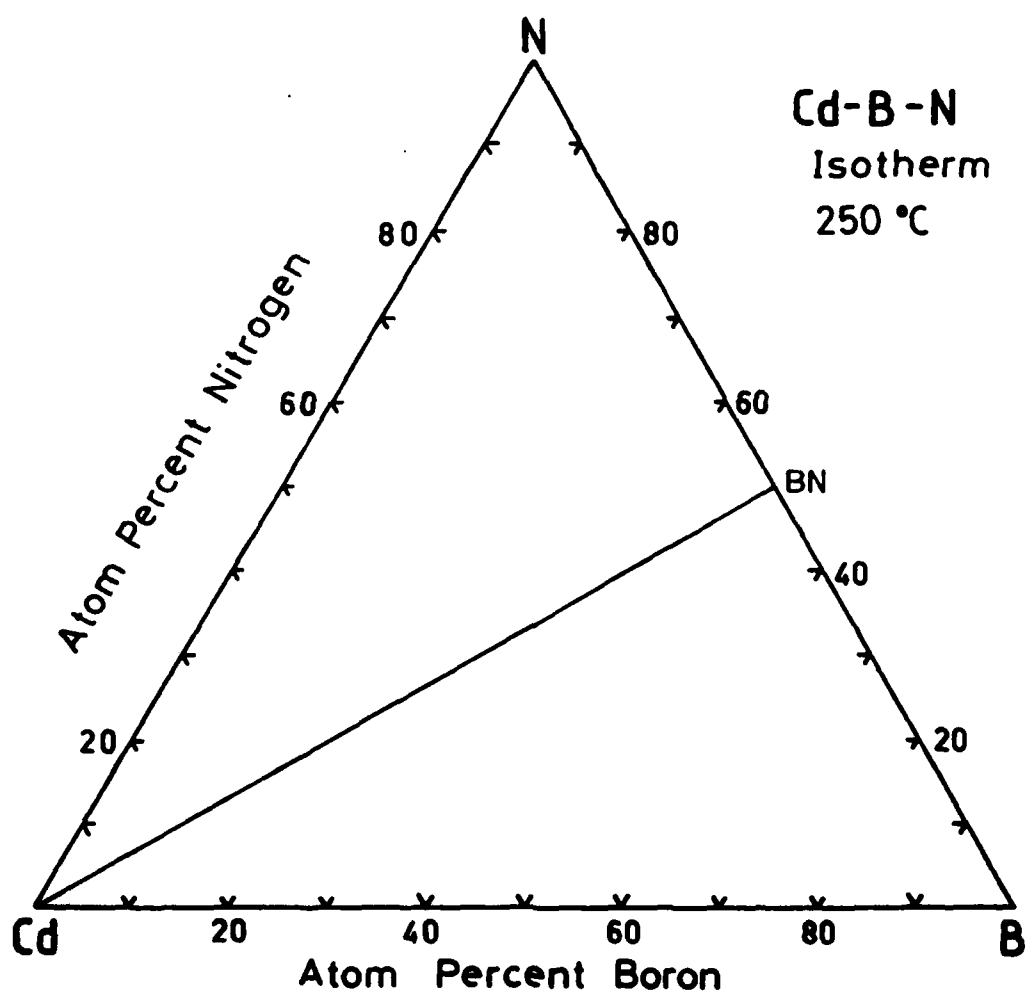
## REFERENCES

- [85Yas] G.A.Yasinskaya, "Reactions of High Melting Compounds with Molten Metals" (in Russian), *Ogneupory* 30 (1985) 20-30
- [77Gur] V.N.Gurin and M.M.Korsukova, "Ib and IIb Subgroup Borides" in "Boron and Refractory Borides" V.N. Matkovich (ed), (Springer, Berlin, Heidelberg, N.Y., 1977) 293-309
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, Oh, 1985)
- [88Wri] H.A.Wriedt, "The N-Cd (Nitrogen-Cadmium) System", *Bull. Alloy Phase Diagrams* 9 (1988) 245-247
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M=Al, Cu, Zn, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi)", *J.Mater.Res.* 5 (1990) 2152-2159
- [90Mas] T.B.Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc. Met., Metals Park, Oh, 1990)

Table 1: Solid phases at 375°C in the system B - Cd - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Cd <321.11°	hP2 P6 <sub>3</sub> /mmc Mg	a= 297.88 c= 561.67	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 866.1	[85Vil]
Cd <sub>3</sub> N <sub>2</sub>	cI80 Ia $\bar{3}$ Mn <sub>2</sub> O <sub>3</sub>	a=1081	[85Vil]
CdN <sub>6</sub>	oP56 Pbca	a= 784 b= 647 c=1607	[88Wri]

Fig.1: Isothermal section at 250°C in the system B - Cd - N



## SYSTEM BORON - ALUMINIUM - NITROGEN (B-Al-N)

### INTRODUCTION / EXPERIMENTAL

Information on the phase relations in the Al-B-N system are due to several research groups [65Pri, 67Lue, 72Lyu, 73Lyu, 79Sir, 81Hir, 82And1, 82And2 and 91Rem]. A recent critical review has been provided by [90Jeh]. General agreement exists on the absence of ternary compounds. Various methods employed such as (a) nitriding of complex salts of Al and B or mixtures of metal and complex salts in  $\text{NH}_3$ , or (b) reaction sintering of polycrystalline samples  $\text{Al}+\text{BN}$ , resulted in the formation of extended solid solutions of the nononitrides  $\text{Al}_{1-x}\text{B}_x\text{N}$  [65Pri, 72Lyu, 73Lyu, 79Sir, 82And1, 82And2, 91Rem].  $\text{AlN}$  was found to act as a catalyst for the synthesis of cubic BN from hexagonal BN in lowering the temperature and pressure conditions to  $1000^\circ\text{C}$  and 7 GPa [81Hir]; sintering of  $\text{BN}+\text{Al}$  powder compacts in the range from 1500 to  $3000^\circ\text{C}$  and 5 to 9.5 GPa resulted in cubic BN with 2-3 mass% Al dissolved [79Sir]. The lattice parameter of BN was said to decrease from 361.5 to 361.0 pm on saturation with Al; higher Al contents yielded the formation of  $\text{AlN}$ ,  $\text{AlB}_{12}$  and  $\beta\text{-B}$  [79Sir]. Two isothermal sections at  $10^5\text{Pa}$  and 8GPa have been presented [73Lya, 79Sir, 82And1, 82And2].

Phase equilibria in the B-Al-N system at  $900^\circ\text{C}$  under  $10^5\text{Pa}$  argon (in the absence of external nitrogen) have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts of B, BN, and of prealloyed binary borides, which prior to use were crushed to a particle size smaller than  $20\mu\text{m}$  in a WC-Co mortar. For annealing the samples were kept on a Mo(or BN)-substrate within a wire resistance heated quartz recipient under argon. Heat treatments usually consisted of total of 1000h with repeated crushing and recompacting to ensure homogeneity [91Rem]. Starting materials were ingots of 3N-Al, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at  $1400^\circ\text{C}$ .

## BINARY SYSTEMS

A tentative phase diagram Al-B as presented in [E11] contains  $\text{AlB}_2$  and  $\text{AlB}_{12}$  as the only binary phases (Table 1) and is in agreement with a reinvestigation at  $900^\circ\text{C}$  [91Rem]. The solid solubility of B in Al is less than 0.025 at%B at  $859.7^\circ\text{C}$ . No attempts have been made to establish the solubility of Al in boron. The assessed version of the Al-B diagram is shown in Fig.1.

The Al-N phase diagram, as suggested by [90Mas], is accepted; a detailed description is due to [86Wri]. AlN is the only binary phase (Table 1). The solid solubility of N in Al is low [86Wri].

## SOLID PHASES / ISOTHERMAL SECTIONS

Fig 2 shows the phase equilibria as determined by [82And2] at a pressure of 8 GPa.

Fig.3 represents the isothermal section at  $900^\circ\text{C}$  (in the absence of external nitrogen pressure). Phase equilibria are characterized by the formation of a stable equilibrium  $\text{AlB}_2 + (\text{AlN}) + (\text{BN})$  with a small but significant mutual solubility of  $\text{Al}_{1-x}\text{B}_x\text{N}_x$ . No ternary compounds have been observed.

## REFERENCES

- [85Pri] L.I.Prihod'ko, "Materials with Special Physical Properties in the Al-B-N System" (in Russian), Vestn.Kiev.Polytkhn.Inst., Mekhan.Tekhnol., 2 (1985) 59-63
- [67Lue] M.Luetkemeyer and K.Kirner, "High Temperature Reactions of BN with A", Prakt.>Metallogr. 4 (1967) 83-87
- [72Lyu] M.D.Lyutaya, T.S.Barnitskaya and I.S.Fainer, "Group IIIA Mixed Nitrides (in Russian), Kristallokhim.Tugoplav. Soedin 53 (1972) 53-61
- [73Lyu] M.D.Lyutaya and T.S.Barnitskaya, "Formation Characteristics and Chemical Stability of Complex Nitrides of Elements of Subgroup IIIB, The System Al-B-N", (in Russian) Izv.Akad. Nauk SSSR, Neorg.Mater. 9 (1972) 1367-1371
- [77Hig] I.Higashi, T.Sakurai and T.Atoda, "Crystal Structure of  $\alpha$ -AlB<sub>12</sub>", J.Solid State Chem. 20 (1977) 67-77
- [79Sir] N.N.Sirota and M.M.Zhuk, "Study of Phase Composition and Some Properties of a Superhard Material Obtained in the Boron Nitride-Aluminium System at High Pressures and Temperature", (in Russian), Vestsi Akad.Nauk Beloruss.SSR,Ser.Fiz.-Mat. 5 (1979) 85-88
- [81Hir] S.Hirano,T.Yamaguchi and S.Naka, "Effects of AlN Additions on the Synthesis of Cubic Boron Nitride", J.Am. Ceram.Soc. 64 (1981) 734-736
- [82And1] T.V.Andreeva, I.I.Timofeeva and T.S.Barnitskaya, "New Boron Containing Phases in the B-N-Al System" (in Russian), Vysiko-Temper.Boridi i Silitsidi (Kiev,1982) 80-82
- [82And2] T.V.Andreeva, T.S.Barnitskaya, A.Butylenko, Yu.M.Goryachev and I.I.Timofeeva, "Effect of Pressure on the Phase Composition in the System B-N-Al", (in Russian), Pritsessy Vzainod.Granitse Razdela Faz., (Kiev,1982) 70-74
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc. Met.,Metals Park,Oh, 1985)
- [86Wri] H.A.Wriedt, "The Al-N System", Bull.Alloy Phase Diagrams 7 (1986) 329-333



[90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met., Metals Park, Oh, 1990)

[91Rem] K.Remschnig, H.Duschaneck and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary System Al-B-N", Research at the University of Vienna (1991)

Table 1: Solid phases at 900°C in the system B-Al-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Al <660.452°	cF4 Fm $\bar{3}$ m Cu	a= 404.96	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
AlB <sub>2</sub> <975°	hP3 P6/mmm AlB <sub>2</sub>	a= 300.6 c= 352.2	[85Vil]
$\gamma$ -AlB <sub>12</sub> (r) <1450°	oP384 P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> $\gamma$ -AlB <sub>12</sub>	a=1657.3 b=1751.0 c=1018.0	[81Hig]
$\alpha$ -AlB <sub>12</sub> (h) 1920-1450°	tP216 P4 <sub>1</sub> 2 <sub>1</sub> 2 $\alpha$ -AlB <sub>12</sub>	a=1015.8 c=1427.0	[77Hig]
AlN	hP4 P6 <sub>3</sub> /mc ZnS	a= 311.14 c= 497.92	[86Wri]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]

Fig.1: The binary system Al-B

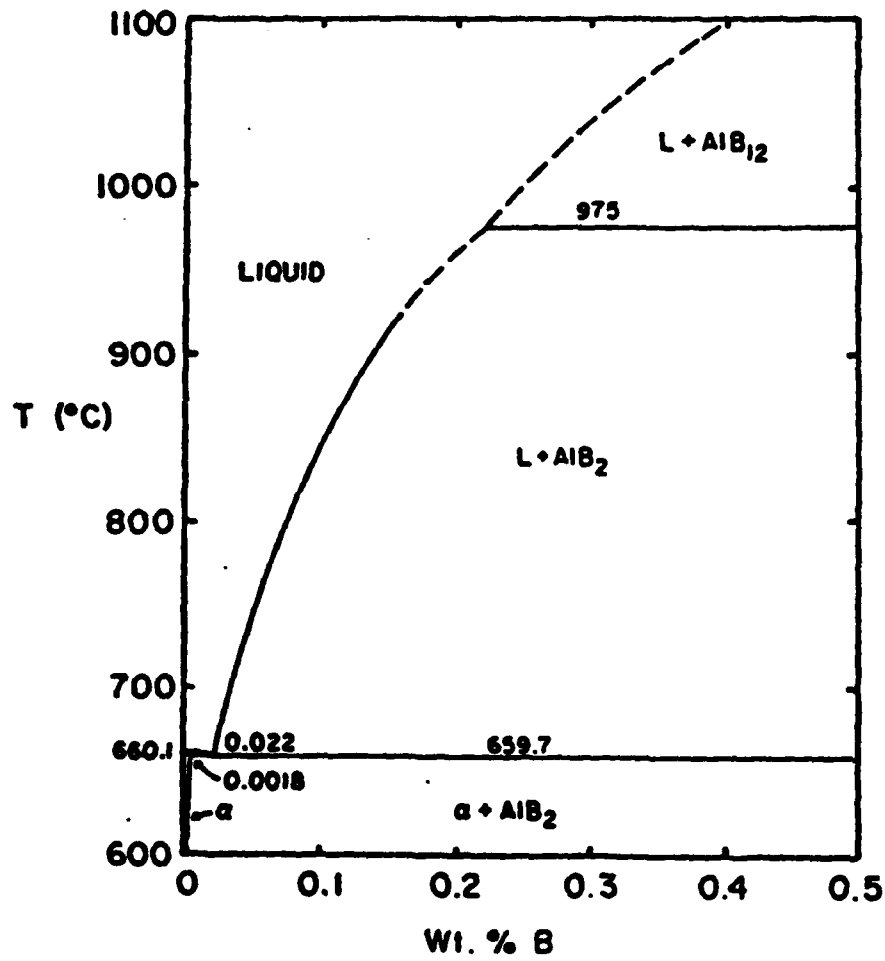


Fig.2: Isothermal section in the system B-Al-N under 8 GPa [82And2]

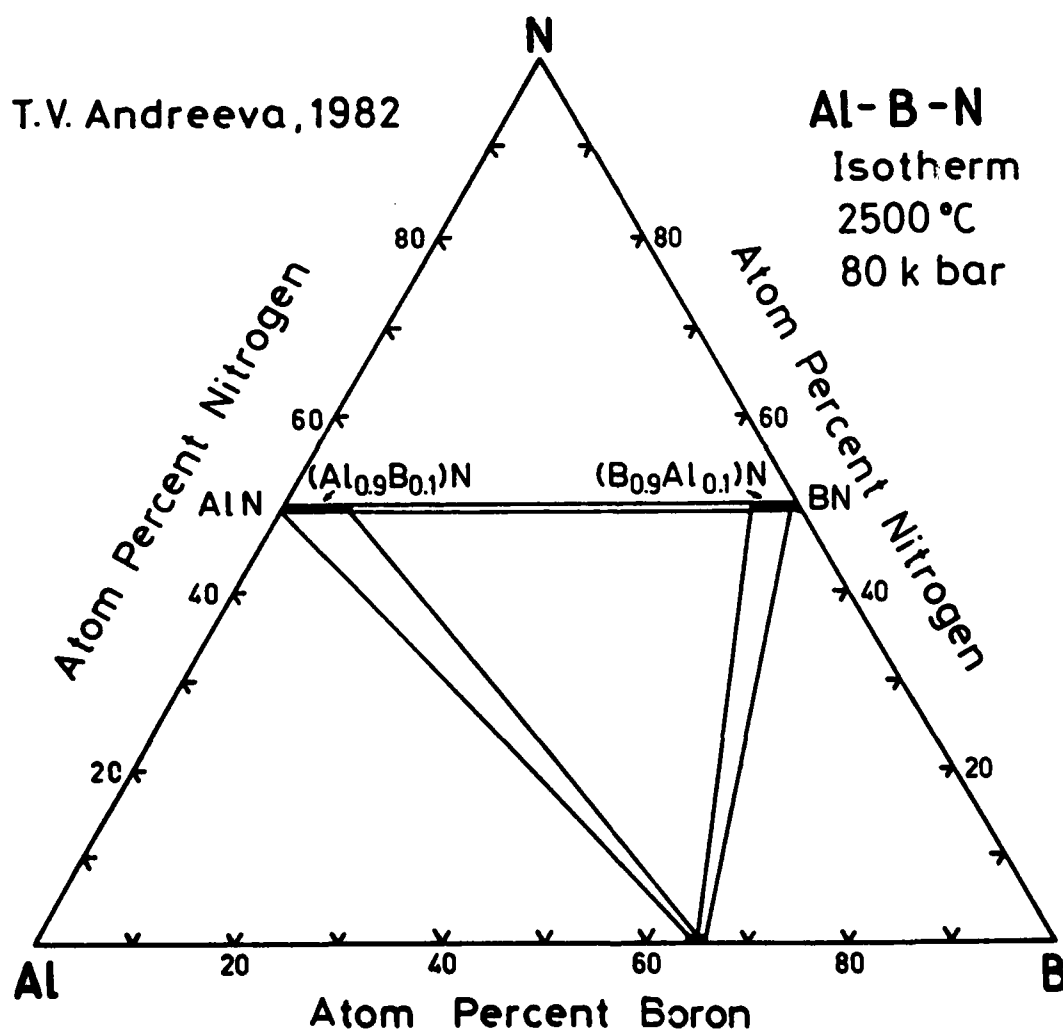
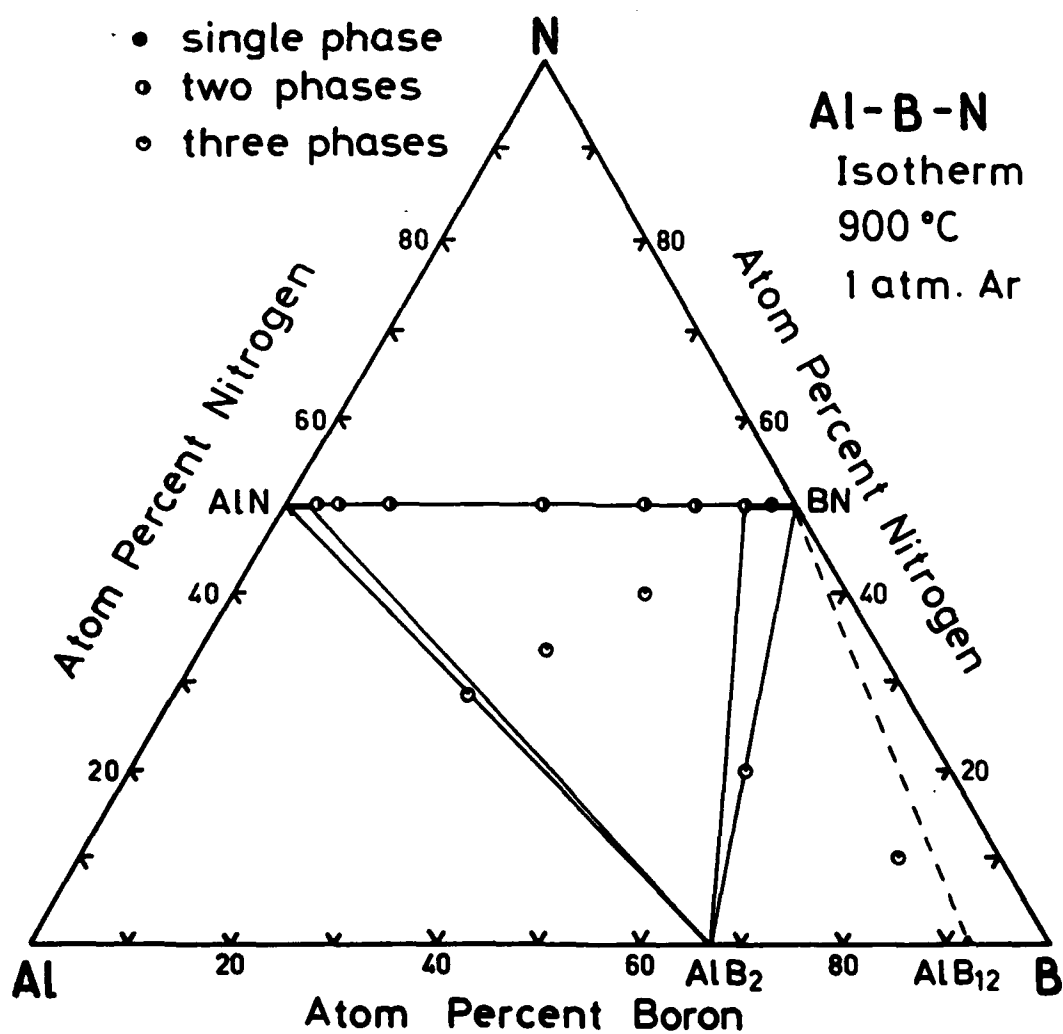


Fig.3: Isothermal section at 900°C in the system B - Al - N  
under  $10^5$  Pa argon, in the absence of external nitrogen



## SYSTEM BORON - INDIUM - NITROGEN (B-In-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-In-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 120°C for a total of 1800h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-In, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C.

### BINARY SYSTEMS

A tentative monotectic type of equilibrium diagram for the system B-In is given in [Mof,65Wal]. There is no binary boride known and there is practically no mutual solid solubility of the elements. No phase diagram In-N exists. According to a critical assessment by [89Ok] the only binary nitride InN was said to be rather unstable and to decompose at ca 680°C under 10<sup>5</sup>Pa N<sub>2</sub> [38Juz], [87Jon]. The interstitial solubility of N in In is likely to be very low; no details are known so far [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 120°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (In) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed [90Wei].

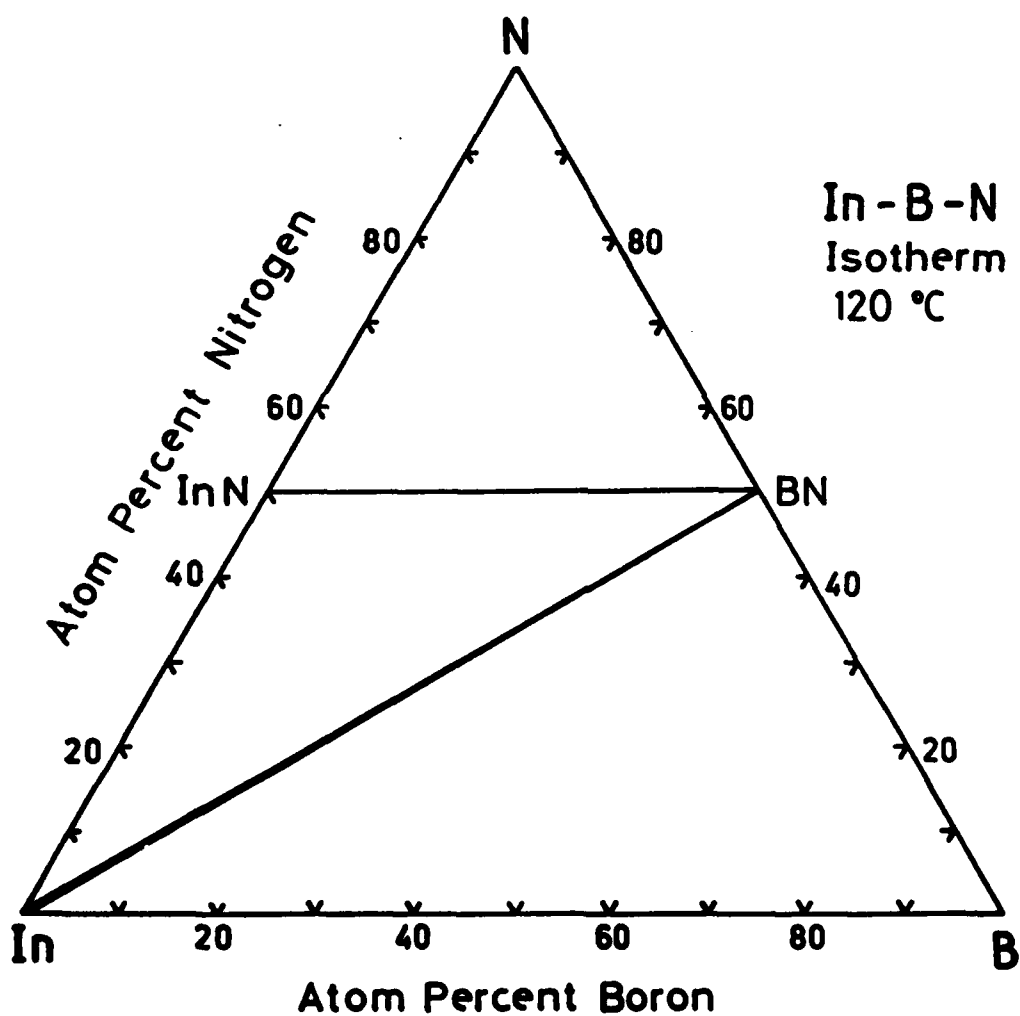
## REFERENCES

- [38Juz] R. Juza and H.Hahn, "On the Crystal Structures of  $\text{Cu}_3\text{N}$ ,  $\text{GaN}$  and  $\text{InN}$ ", *Z.Anorg.Allg. Chemie* 239 (1938) 282-287
- [65Wal] F. Wald and R.W.Stormont, "Investigations on the Constitution of Certain Binary Boron-Metal Systems", *J. Less Common Met.* 9 (1965) 423-433
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc. Met., Metals Park, Oh, 1985)
- [87Jon] R.D.Jones and K.Rose, "Thermal Stability of  $\text{InN}$ ", *J.Phys.Chem. Solids* 48 (1987) 587-590
- [89Oka] H.Okamoto, "The In-N System", *Bull.Alloy Phase Diagrams* 10 (1989) 656
- [90Mas] T.B.Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met., Metals Park, Oh, 1990)
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M=Al,Cu,Zn,Ag,Cd,In,Sn,Sb,Au,Tl,Pb,Bi)", *J.Mater.Res.* 5 (1990) 2152-2159

Table 1: Solid phases at 120°C in the system B-In-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
In <156.63°	tI2 I4/mmm In	a= 325.3 c= 494.70	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}m$ $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
InN	hP4 P6 <sub>3</sub> mc ZnS	a= 354.0 c= 570.4	[85Vil]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section at 120°C in the system B - In - N





## SYSTEM BORON - THALLIUM - NITROGEN (B-Tl-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Tl-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 200°C for a total of 1000h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were ingots of 3N-Tl, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C.

### BINARY SYSTEMS

A tentative monotectic type of equilibrium diagram for the system B-Tl is given in [Mof,65Wal]. There is no binary boride known and there is practically no mutual solid solubility of the elements. No phase diagram is available for Tl-N. The binary nitrides TlN and TlN<sub>2</sub> were said to be rather unstable. TlN is obtained in the arc using Tl-electrodes under nitrogen [76Fro]. According to thermal expansion data in the range from 95 to 600 K, TlN<sub>2</sub> was observed with three modifications [73Mau]. TlN<sub>2</sub> at room temperature was reported to be isomorphic with KN<sub>2</sub>:  $\beta$ -TlN<sub>2</sub> (tI16 - I4/mcm,  $a=620.94$ ,  $c=735.83\text{pm}$  [73Mau]) with a transition into an orthorhombic structure at temperatures below 248(5)K:  $\alpha$ -TlN<sub>2</sub> (oP32,  $a=871.8$ ,  $b=876.6$ ,  $c=739.5\text{pm}$  [73Mau]); furthermore a cubic high temperature phase  $\gamma$ -TlN<sub>2</sub> (Pm $\bar{3}$ m, structure unknown) has been discussed to be stable at 10<sup>5</sup>Pa N<sub>2</sub> above 565.2 K; see [73Mau]. No interstitial solubility of N in Tl was observed up to 600°C [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 200°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Tl) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed.

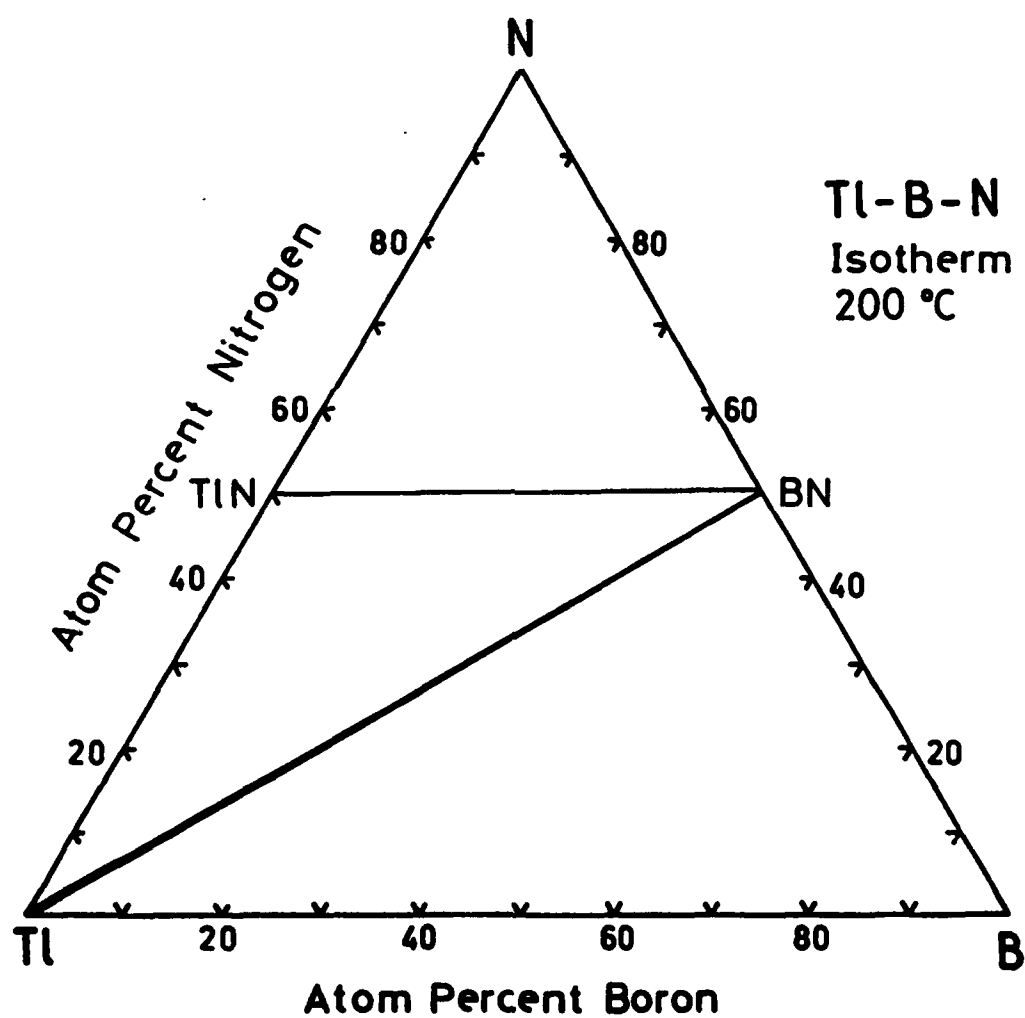
## REFERENCES

- [65Wal] F.Wald and R.W.Stormont, "Investigations on the Constitution of Certain Binary Boron-Metal Systems", J. Less Common Met. 9 (1965) 423-433
- [73Mau] F.A.Mauer, C.R. Hubbard and T.A.Hahn, "Thermal Expansion and Low Temperature Phase Transition of Thallous Azide", J.Chem.Phys., 59 (1973) 3770-3776
- [77Gur] V.N.Gurin and M.M.Korsukova, " Ib and IIb Subgroup Borides " in " Boron and Refractory Borides ", V.N.Matkovich (ed), (Springer,Berlin,Heidelberg,N.Y.,1977) 293-309
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc. Met.,Metals Park,Oh, 1985)
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met., Metals Park,Oh, 1990)
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M=Al,Cu,Zn,Ag,Cd,In,Sn,Sb,Au,Tl,Pb,Bi)", J.Mater.Res. 5 (1990) 2152-2159

Table 1: Solid phases at 200°C in the system B-Tl-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\alpha$ -Tl <230°	hP2 P6 <sub>3</sub> /mmc Mg	a= 345.66 c= 552.48	[90Mas]
$\beta$ -Tl <303°	cI2 Im $\bar{3}$ m W	a= 387.1	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil]
TlN	hP4 P6 <sub>3</sub> mc ZnS	a= 368 c= 601	[85Vil]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]

Fig.1: Isothermal section at 200°C in the system B - Tl - N



## SYSTEM BORON - TIN - NITROGEN (B-Sn-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Sn-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 200°C for a total of 1100h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-Sn, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C.

### BINARY SYSTEMS

A tentative monotectic type of equilibrium diagram for the system B-Sn is given in [Mof], for a more detailed discussion see [77Mak]. There is no binary boride known and there is practically no mutual solid solubility of the elements. No phase diagram exists for N-Sn. Binary nitrides  $\text{Sn}_3\text{N}_4$  and  $\text{Sn}_3\text{N}_2$  were said to be rather unstable and may be prepared by heating  $\text{Sn}(\text{NH}_2)_2\text{Cl}$  or  $\text{SnNH}$  to 340°C in vacuum. In the temperature range 25° to 800°C the interstitial solubility of N in Sn is said to be negligible [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 200°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by compatibility of (Sn) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed in agreement with an earlier preliminary investigation of the reaction  $(\text{l-Sn}) + \text{BN}$  at 800°C [65Yas].

### MISCELLANEOUS

Nonwetting behavior ( $\theta > 90^\circ$ ) was claimed by [65Yas].

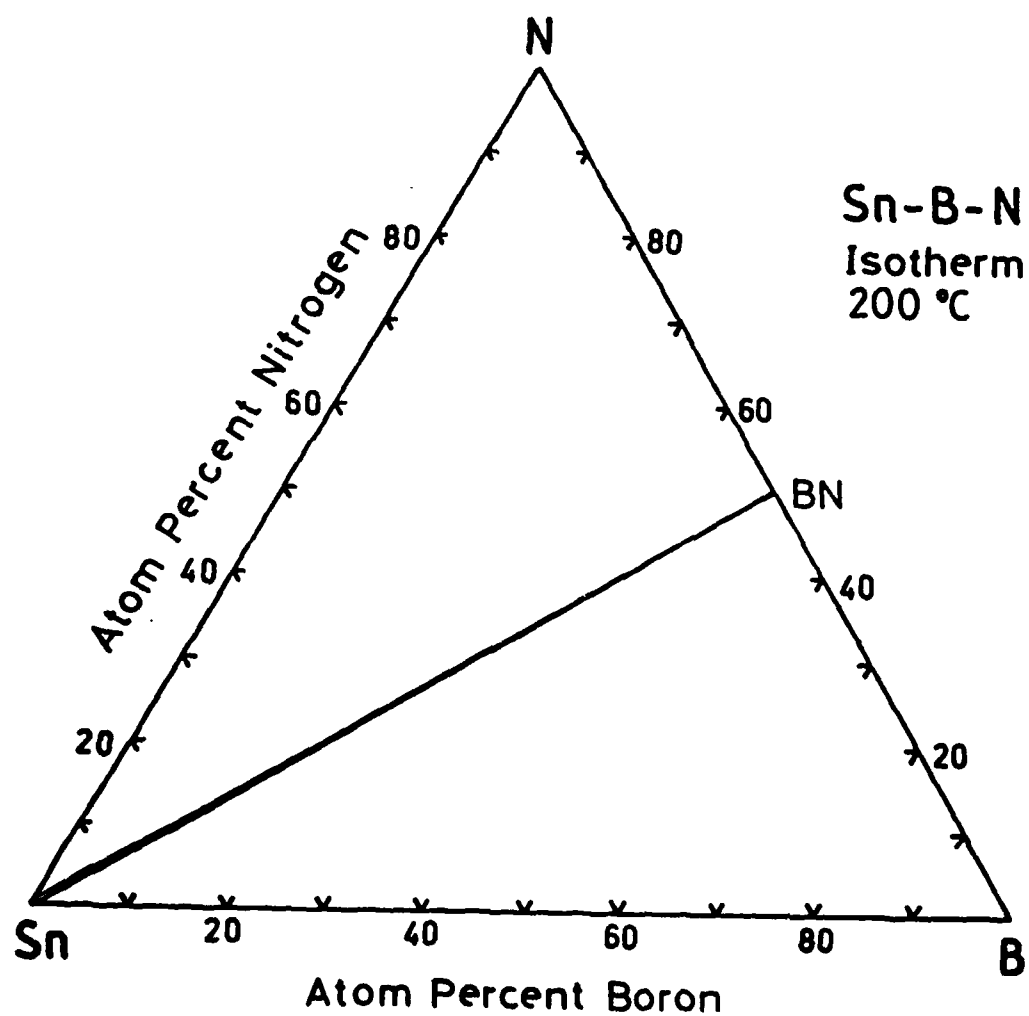
## REFERENCES

- [65Yas] G.A.Yasinskaya, "Reactions of High Melting Compounds with Molten Metals" (in Russian), *Ogneupory* 30 (1965) 20-30
- [77Gur] G.N.Makarenko, "Borides of the IVb Group "in " Boron and Refractory Borides ", V.N.Matkovich (ed),(Springer,Berlin, Heidelberg,N.Y.,1977) 310-330
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc. Met.,Metals Park,Oh, 1985)
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met., Metals Park,Oh, 1990)
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M=Al,Cu,Zn,Ag,Cd,In,Sn,Sb,Au,Tl,Pb,Bi)", *J.Mater.Res.* 5 (1990) 2152-2159

Table 1: Solid phases at 200°C in the system B-Sn-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
$\beta$ -Sn <231.97°	tI4 I4 <sub>1</sub> /and $\beta$ -Sn	a= 583.18 c= 318.18	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 688.1	[85Vil]

Fig.1: Isothermal section at 200°C in the system B - Sn - N



## SYSTEM BORON - LEAD - NITROGEN (B-Pb-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Pb-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 200°C for a total of 1500h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were ingots of 3N-Pb, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C.

### BINARY SYSTEMS

A tentative monotectic type of equilibrium diagram for the system B-Pb is given in [Mof]; a comprehensive discussion of all reported information has been given by [77Mak]. There is no binary boride known and there is practically no solid solubility of B in Pb. In the Pb-N system several rather unstable binary compounds have been claimed to exist:  $Pb_3N_2$  and  $Pb_3N_4$ , which have been prepared by cathodic sputtering [76Fro], and metastable  $PbN_6$ , for which two structural modifications have been reported (Table 1). There is practically no solubility of N in Pb up to 600°C [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 200°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Pb) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed in agreement with an earlier preliminary investigation of the reaction (l-Pb) + BN at 800°C [65Yas].



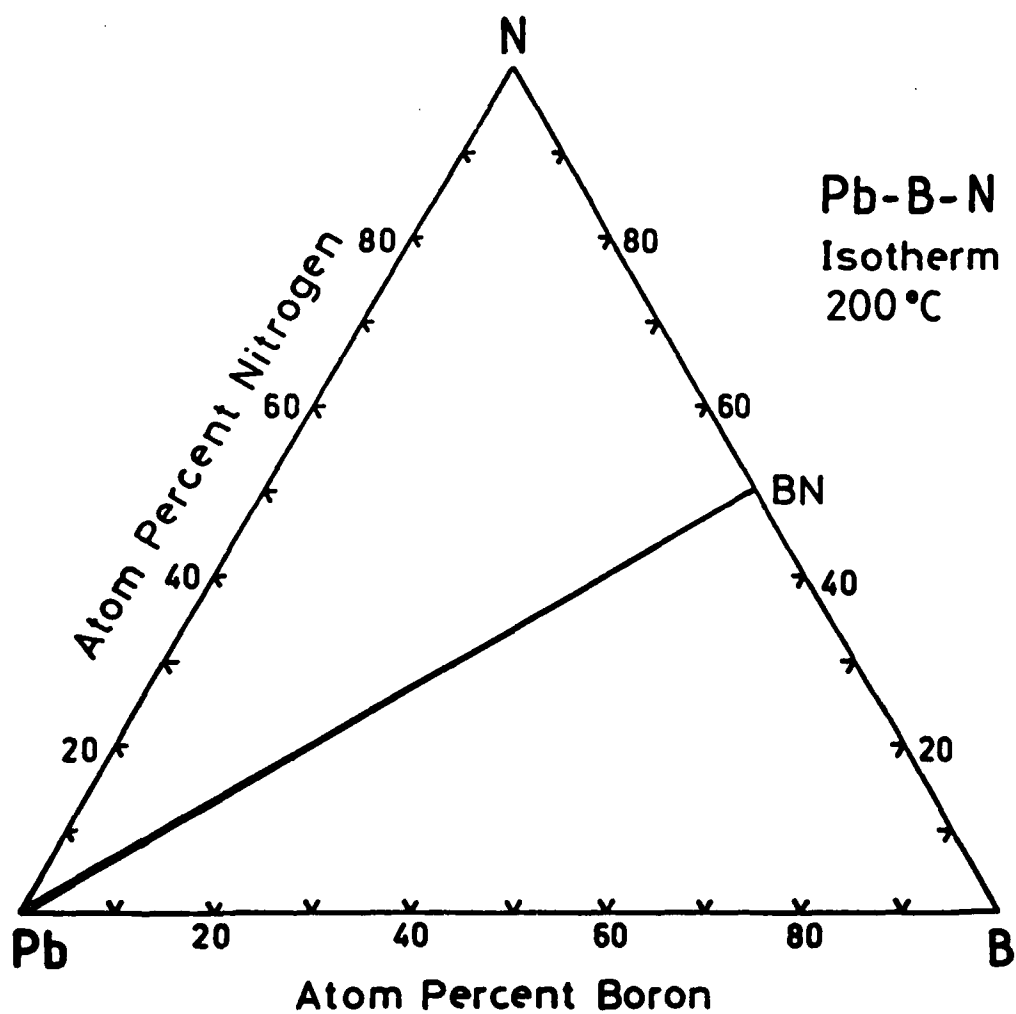
## REFERENCES

- [85Yas] G.A.Yasinskaya, "Reactions of High Melting Compounds with Molten Metals" (in Russian), *Ogneupory* 30 (1965) 20-30
- [77Mak] G.N.Makarenko, "Borides of the IVb Group" in " Boron and Refractory Borides ", V.N.Matkovich (ed),(Springer,Berlin, Heidelberg,N.Y.,1977) 310-330
- [85Vil] P.Villars and L.D.Calvert,"Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc. Met.,Metals Park,Oh, 1985)
- [90Mas] T.B.Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met., Metals Park,Oh, 1990)
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M=Al,Cu,Zn,Ag,Cd,In,Sn,Sb,Au,Tl,Pb,Bi)", *J.Mater.Res.* 5 (1990) 2152-2159

Table 1: Solid phases at 200°C in the system B-Pb-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Pb <327.50°	cF4 Fm $\bar{3}$ m Cu	a= 495.02	[90Mas]
$\beta$ -rhB <2092°	hR111 R $\bar{3}$ m $\beta$ -B	a=1092.51 c=2381.43	[85Vil]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]
$\alpha$ -PbN <sub>6</sub>	oP84 Pnma	a= 663 b=1625 c=1131	[85Vil]
$\beta$ -PbN <sub>6</sub>	monoclinic	a= 509.0 b=8844 c=1750.8 $\beta$ =90.016° a=1849 b= 884 c= 512 $\beta$ =107.583°	[E11] or [E11]

Fig.1: Isothermal section at 200°C in the system B - Pb - N



## SYSTEM - BORON - ANTIMONY - NITROGEN (B-Sb-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Sb-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 575°C for a total of 900h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-Sb, crystallized boron (99.8 % B), hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C.

### BINARY SYSTEMS

A tentative monotectic type of equilibrium diagram for the system B-Sb is given in [Mof,65Wal]. There is no binary boride known and there is practically no mutual solid solubility of the elements. No phase diagram is available for N-Sb and no binary nitrides of Sb have been reported. The solubility of N in Sb is likely to be very low.

### SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 575°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Sb) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed [90Wei].

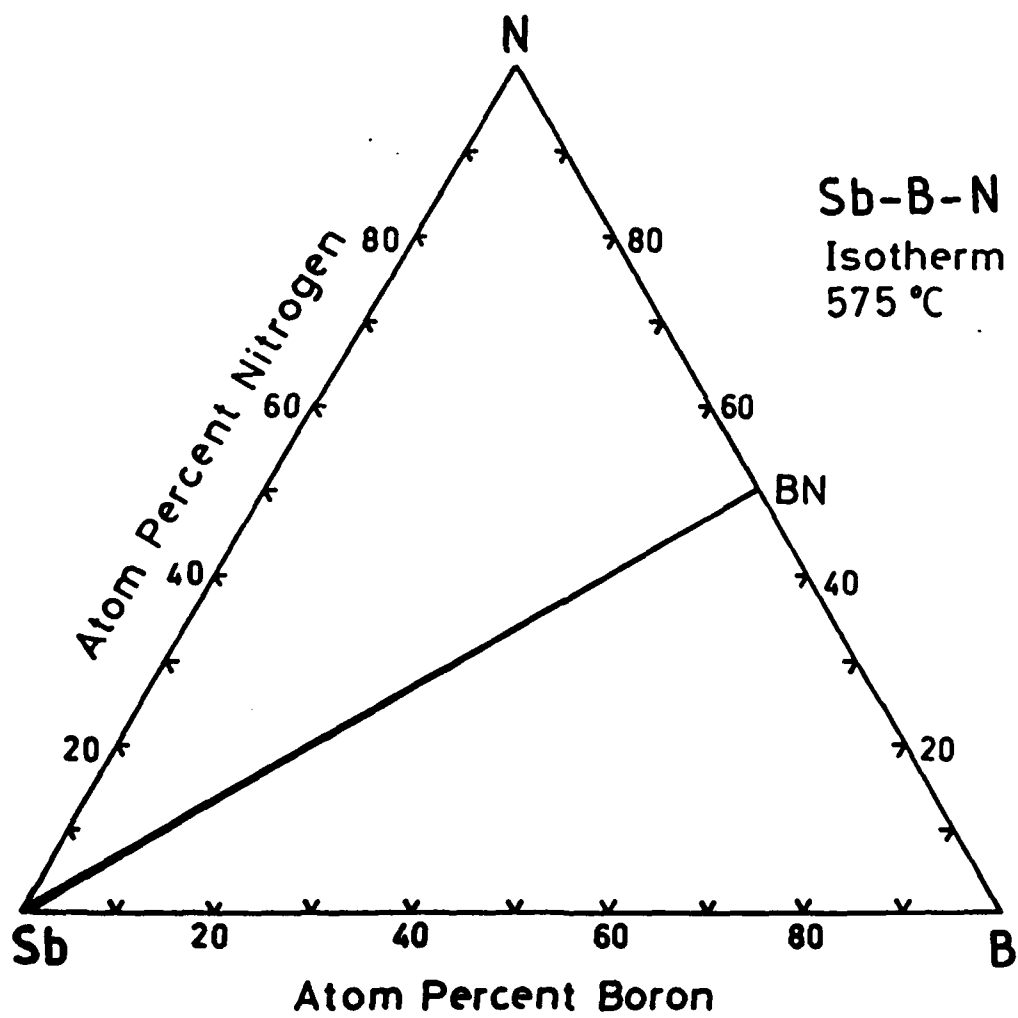
## REFERENCES

- [65Wal] F.Wald and R.W.Stormont, "Investigations on the Constitution of Certain Binary Boron-Metal Systems", J. Less Common Met. 9 (1965) 423-433
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc. Met., Metals Park, Oh, 1985)
- [90Mas] T.B.Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met., Metals Park, Oh, 1990)
- [90Wei] F.Weitzer, K.Remschig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M=Al,Cu,Zn,Ag,Cd,In,Sn,Sb,Au,Tl,Pb,Bi)", J.Mater.Res. 5 (1990) 2152-2159

Table 1: Solid phases at 200°C in the system B-Sn-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Sb <630.78°	hR2 R $\bar{3}m$ $\alpha$ -As	a= 430.84 c=1127.40	[85Vil]
$\beta$ -rhB <2092°	hR111 R $\bar{3}m$ $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 866.1	[85Vil]

Fig.1: Isothermal section at 575°C in the system B - Sb - N



## SYSTEM BORON - BISMUTH - NITROGEN (B-Bi-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria in the B-Bi-N system have been established from X-ray powder diffraction analysis of samples prepared by reaction sintering of powder compacts, which were wrapped in protective Mo-foil, sealed in evacuated silica tubes and annealed at 200°C for a total of 1500h with repeated crushing and recompacting to ensure homogeneity [90Wei]. Starting materials were powders of 3N-Bi, crystallized boron (99.8 % B), and hexagonal boron nitride of 99 % nominal purity, which prior to use was outgassed in high vacuum at 1400°C.

### BINARY SYSTEMS

A tentative monotectic type of equilibrium diagram for the system B-Bi is given in [Mof,65Wal]. There is no binary boride known and there is practically no mutual solid solubility of the elements. No phase diagram Bi-N exists, however, the formation of a binary nitride BiN was claimed without further details [78Fro]. In the temperature range 25° to 800°C there is practically no solubility of N in Bi [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

Fig.1 represents the isothermal section at 200°C (in the absence of external nitrogen pressure). Phase equilibria are characterized by the compatibility of (Bi) and boron nitride with no mutual solid solubility as indicated from X-ray powder analysis. No ternary compounds have been observed in agreement with an earlier preliminary investigation of the reaction (l-Bi) + BN at 800°C [65Yas].

### MISCELLANEOUS

Nonwetting behavior ( $\theta > 90^\circ$ ) was claimed by [65Yas].

## REFERENCES

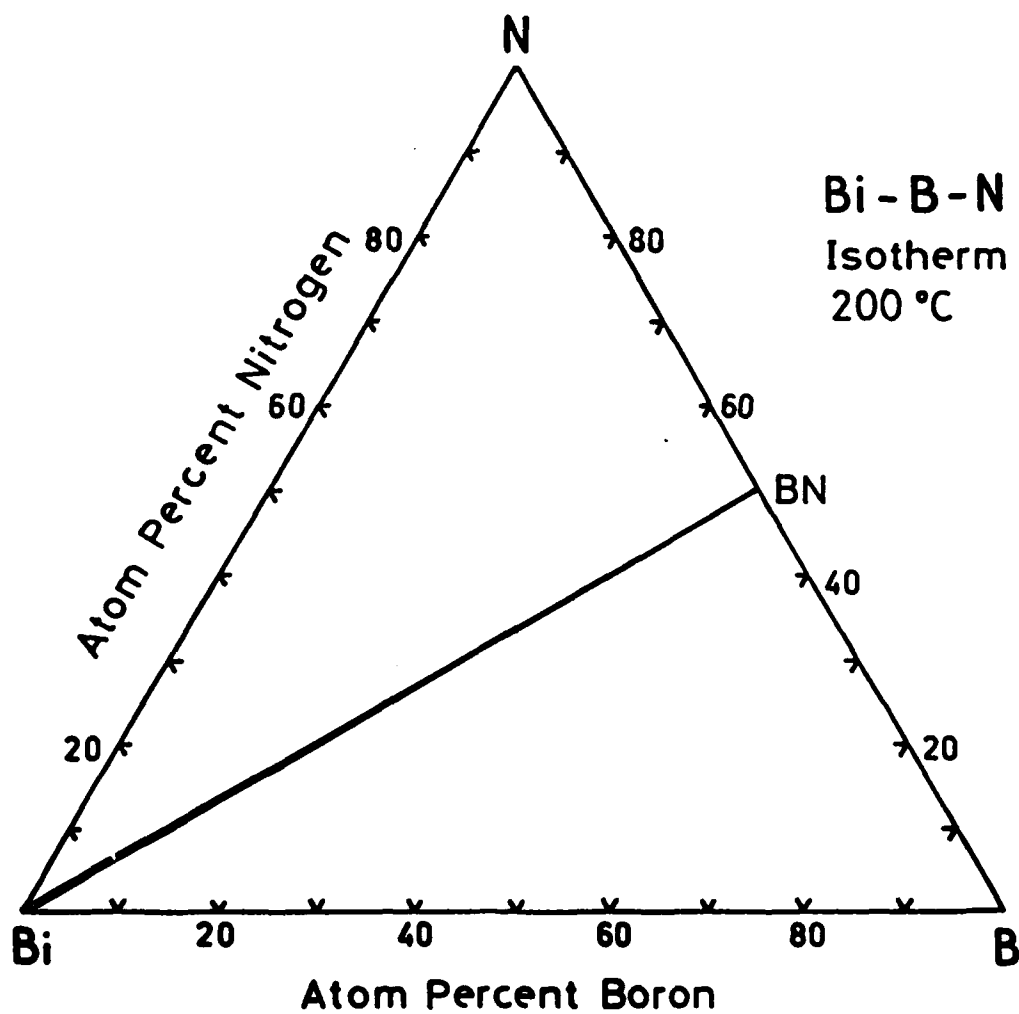
- [65Yas] G.A.Yasinskaya, "Reactions of High Melting Compounds with Molten Metals" (in Russian), *Ogneupory* 30 (1965) 20-30
- [65Wal] F.Wald and R.W.Stormont, "Investigations on the Constitution of Certain Binary Boron-Metal Systems", *J.Less Common Met.* 9 (1965) 423-433
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc. Met., Metals Park, Oh, 1985)
- [90Mas] T.B. Massalski (ed), "Binary Alloy Phase Diagrams", 2<sup>nd</sup> Ed., (Amer.Soc.Met., Metals Park, Oh, 1990)
- [90Wei] F.Weitzer, K.Renschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M=Al,Cu,Zn,Ag,Cd,In,Sn,Sb,Au,Tl,Pb,Bi)", *J.Mater.Res.* 5 (1990) 2152-2159

Table 1: Solid phases at 200°C in the system B-Sn-N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters ( pm )	Comments
Bi <271.44°	hR2 R $\bar{3}m$ $\alpha$ -As	a= 454.60 c=1186.2	[85Vil]
$\beta$ -rhB <2092°	hR111 R $\bar{3}m$ $\beta$ -B	a=1092.51 c=2381.43	[85Vil] [85Vil]
BN <sub>hex</sub>	hP* P6 <sub>3</sub> /mmc BN <sub>hex</sub>	a= 250.4 c= 666.1	[85Vil]



Fig.1: Isothermal section at 200°C in the system B - Bi - N



Part B

Ternary Systems : Metal - Silicon - Nitrogen

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## SYSTEM LITHIUM - SILICON - NITROGEN (Li-Si-N)

### INTRODUCTION / EXPERIMENTAL

Six ternary phases are reported to exist in the system Li-Si-N [53Juz],[70Lan],[87Yam]. In the latter work the phases were synthesized by heating mixtures of  $\text{Li}_3\text{N}$  (prepared from lithium (purity: 2N; from Wako Pure Chemical Ind.Ltd., Japan) and nitrogen (purity: 5N)) and  $\text{Si}_3\text{N}_4$  (UBE-SN-E 10 containing 2 wt% oxygen; from Ube Ind. Ltd., Japan) under nitrogen at  $T \geq 800^\circ\text{C}$  for 24h and more.

### BINARY SYSTEMS

The phase diagram for the system Li-Si due to [85Mar] is reported in [76Mof]. Crystal structures of the intermediate phases are listed in tab.1.1. The diagram for Li-N is given in [86Mas].  $\text{Li}_3\text{N}$  is the only stable nitride (tab.1.1). In addition, the azide  $\text{LiN}_3$  is structurally characterized. No phase diagram is reported for Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.1.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

Only the section  $\text{Li}_3\text{N-Si}_3\text{N}_4$  of the system Li-Si-N was investigated [53Juz],[70Lan][87Yam]. At  $800^\circ\text{C}$  the sequence of coexisting phases is  $\text{Si}_3\text{N}_4 - \text{Li}_2\text{SiN}_2 - \text{Li}_3\text{SiN}_3 - \text{Li}_{10}\text{Si}_2\text{N}_{10} - \text{Li}_{21}\text{Si}_3\text{N}_{11} - \text{Li}_8\text{SiN}_4 - \text{Li}_3\text{N}$  [87Yam]. Crystal structure data of these phases are given in tab.1.1. It should be noted, that the phase labeled  $\text{Li}_8\text{SiN}_4$  by [53Juz] was identified as  $\text{Li}_{21}\text{Si}_3\text{N}_{11}$  by [87Yam] and the phase labeled  $\text{Li}_8\text{SiN}_4$  by [70Lan] was identified as  $\text{Li}_{10}\text{Si}_2\text{N}_{10}$  by [87Yam]. A sixth ternary phase,  $\text{LiSi}_2\text{N}_3$ , was observed at  $1200^\circ\text{C}$  by [87Yam] and at above  $750^\circ\text{C}$  by [70Lan].

### REFERENCES

- [53Juz] R. Juza, H.H. Weber and E. Meyer-Simon, "On Ternary Nitrides and Oxynitrides of Elements of Group 4", Z. Anorg. Allg. Chem. 273 (1953) 48-64

- [70Lan] J.Lang and J.P.Charlot,"The System  $\text{Li}_3\text{N}-\text{Si}_3\text{N}_4$ ", Rev.Chim.Miner. 7 (1970) 121-131
- [76Fro] E.Fromm and E.Gebhardt,"Gase und Kohlenstoff in Metallen" (Springer,Berlin,1976)
- [76Mof] W.Moffatt,"The Handbook of Binary Phase Diagrams", (General Electric Corp.,Schenectady,NY.,1976 and updates)
- [85Mar] C.van der Marel,G.J.B.Vinke and W.van der Lugt,"The Phase Diagram of the System Lithium-Silicon",Solid State Comm. 54 (1985) 917-919
- [85Vil] P.Villars and L.D.Calvert,"Pearsons Handbook of Crystallographic Data for Intermetallic Phases"(Amer.Soc.Met.,Metals Park,OH., 1985)
- [86Mas] T.B.Massalski (ed.),"Binary Alloy Phase Diagrams" (Amer.Soc. Met.,Metals Park,OH.,1986)
- [87Yam] H.Yamane,S.Kikkawa and M.Koizumi,"Preparation of Lithium Silicon Nitrides and their Lithium Ion Conductivity",Solid State Ionics 25 (1987) 183-191

Table 1.1: Solid phases in the system Li - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Li	cI2 Im $\bar{3}$ m W (A2)	a= 351.0	[85Vil];powder pattern: ASTM file card # 15-401
$\text{Li}_{22}\text{Si}_5$	cF432 F23 $\text{Li}_{22}\text{Pb}_5$	a= 1875	[85Vil];powder pattern: ASTM file card # 18-747
$\text{Li}_8\text{Si}_4$ ( $\text{Li}_4\text{Si}_2$ )	oP34 Pbam $\text{Li}_{12}\text{Si}_4$	a= 799 b= 1521 c= 443	[85Vil];powder pattern: ASTM file card # 29-830
$\text{Li}_7\text{Si}_3$	hR7 $\text{R}\bar{3}\text{m}$ $\text{Li}_7\text{Si}_3$	a= 443.5 c= 1813.5	[85Vil]
$\text{Li}_{12}\text{Si}_7$	oP152 Pnma $\text{Li}_{12}\text{Si}_7$	a= 861.0 b= 1973.8 c= 1434.1	[85Vil]



Tab.1.1 continued

$\text{Li}_3\text{N}$	hP4	a= 364.8	[85Vil]; powder pattern:
	P6/mmm	c= 387.5	ASTM file card # 30-759
	$\text{Li}_3\text{N}$		
$\text{LiN}_3$	mC8	a= 562.7	[85Vil]; powder pattern
	C2/m	b= 331.9	ASTM file card # 22-680
	AuSe	c= 497.9	
		$\beta = 107.4^\circ$	
Si	cF8	a= 542.86	[85Vil]; powder pattern:
	Fd $\bar{3}$ m		ASTM file card # 5-565
	C (A4)		
$\alpha\text{-Si}_3\text{N}_4$	hP28	a= 781.8	[85Vil]; powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
$\beta\text{-Si}_3\text{N}_4$	$\text{Si}_3\text{N}_4$		
	hP14	a= 760.8	[85Vil]; powder pattern:
	P6 $_3$ /m	c= 291.1	ASTM file card # 29-1132
$*\text{LiSi}_2\text{N}_3$	$\text{Si}_3\text{N}_4$		33-1160
	oC24	a= 918.6	[85Vil]; powder pattern:
	Cmc2 $_1$	b= 530.2	ASTM file card # 26-1186
	$\text{Cu}_2\text{S}_2\text{Si}$	c= 477.6	
$*\text{Li}_2\text{SiN}_2$			[70Lan]; powder pattern:
			ASTM file card # 23-365
$*\text{Li}_3\text{SiN}_3$	cI96	a= 472.40	[87Yam];
	Ia $\bar{3}$		gives powder pattern
	$\text{AlLi}_3\text{N}_2$ (E9 $_d$ )		
$*\text{Li}_{1.8}\text{Si}_{1.2}\text{N}_{3.0}$	t**	a= 1416.8	[87Yam]; powder pattern:
		c= 1435.3	ASTM file card # 23-366
$*\text{Li}_{2.1}\text{Si}_{1.9}\text{N}_{3.1}$			and in [78Yam]
	t**	a= 947.0	[87Yam]; powder pattern:
		c= 953.0	ASTM file card # 7-260
$*\text{Li}_3\text{SiN}_4$			and in [87Yam]
	t**	a= 1021.7	[70Lan]; powder pattern:
		c= 953.6	given in [87Yam]

## SYSTEM BERYLLIUM - SILICON - NITROGEN (Be-Si-N)

### INTRODUCTION / EXPERIMENTAL

Seven ternary phases are reported to exist in the system Be-Si-N [60Rab],[67-1Eck],[67-2Eck],[75Hus],[77Tho],[80Sch]. In the latter work the samples were prepared from beryllium nitride (reactor quality; from Serva Int., FRG) and silicon nitride (HCST 3733 containing 1.2 wt% carbon, 2.1 wt% oxygen, 38.7 wt% nitrogen; from H.C. Starck Berlin, FRG) by hot pressing ( $28 \text{ MN/m}^2$ ) under nitrogen at  $1760^\circ\text{C}$  for 45'.

### BINARY SYSTEMS

The phase diagram for the system Be-Si is given in [86Mas]. No phase diagrams are reported for Be-N or Si-N.  $\text{Be}_3\text{N}_2$  as well as  $\text{Si}_3\text{N}_4$  exist in two modifications (tab. 2.1). Under  $10^5 \text{ Pa N}_2$   $\text{Be}_3\text{N}_2$  melts at  $2200^\circ\text{C}$  [87Wri]. The solubility of nitrogen in silicon as well as in beryllium is very low [76Fro][87Wri].

### SOLID PHASES / ISOTHERMAL SECTIONS

Only the section  $\text{Be}_3\text{N}_2\text{-Si}_3\text{N}_4$  of the system Be-Si-N was investigated [60Rab],[67-1Eck],[67-2Eck],[75Hus],[76Tho],[77Tho],[80Sch]. The ternary phases found can be described by the general formula  $\text{Be}_{3+n}\text{Si}_n\text{N}_{4+n}$ . At  $1760^\circ\text{C}$  the sequence of coexisting phases is  $\text{Si}_3\text{N}_4$  -  $\text{BeSiN}_2$  ( $n=\infty$ ) -  $\text{Be}_6\text{Si}_6\text{N}_{10}$  ( $n=6$ ) -  $\text{Be}_{11}\text{Si}_5\text{N}_{14}$  ( $n=5$ ) -  $\text{Be}_5\text{Si}_2\text{N}_8$  ( $n=4$ ) -  $\text{Be}_9\text{Si}_3\text{N}_{10}$  ( $n=3$ ) -  $\text{Be}_4\text{SiN}_4$  ( $n=2$ ) -  $\text{Be}_7\text{SiN}_6$  ( $n=1$ ) -  $\beta\text{-Be}_3\text{N}_2$  [80Sch]. Crystal structure data of these phases are given in tab. 2.1.  $\beta\text{-Be}_3\text{N}_2$  dissolves 2.5 mol%  $\text{Si}_3\text{N}_4$  [80Sch].

### REFERENCES

- [60Rab] A. Rabenau and P. Eckerlin, "Compounds in the System  $\text{Be}_3\text{N}_2\text{-Si}_3\text{N}_4$ ", in "Special Ceramics", P. Popper (ed.) (Heywood & Co, London, 1960) p136-143
- [67-1Eck] P. Eckerlin, A. Rabenau and H. Nortmann, "Preparation and Properties of  $\text{BeSiN}_2$ ", Z. Anorg. Allg. Chem. 353 (1967) 113-121

- [67-2Eck] P.Eckerlin, "The Crystalstructure of  $\text{BeSiN}_2$ ", *Z.Anorg.Allg. Chem.* **353** (1967) 225-235
- [75Hus] I.C.Huseby, H.K.Lukas and G.Petzow, "Phase Equilibria in the System  $\text{Si}_3\text{N}_4$ - $\text{SiO}_2$ - $\text{BeO}$ - $\text{Be}_3\text{N}_2$ ", *J.Amer.Ceram.Soc.* **58** (1975) 377-380
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [76Tho] D.P.Thompson, "New Polytypes in the Be-Si-O-N System", *J.Mater. Sci.* **11** (1976) 1377-1380
- [77Tho] D.P.Thompson and L.J.Gaukler, "Further Study of the Be-Si-O-N Polytypes", *J.Amer.Ceram.Soc.* **60** (1977) 470-471
- [80Sch] G.Schneider, L.J.Gaukler and G.Petzow, "Phase Equilibria in the System  $\text{AlN}$ - $\text{Si}_3\text{N}_4$ - $\text{Be}_3\text{N}_2$ ", *J.Amer.Ceram.Soc.* **63** (1980) 32-35
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [87Wri] H.A.Wriedt, "The Be-Si (Beryllium-Silicon) System", *Bull.Alloy Phase Diagr.* **8** (1987) 136-139

Table 2.1: Solid phases in the system Be - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\alpha$ -Be(r) T<1270	hP2 P6 <sub>3</sub> /mmc Mg (A3)	a= 228.58 c= 358.43	[85Vil]; powder pattern: ASTM file card # 22-111
$\beta$ -Be(h) T>1270	cI2 Im $\bar{3}$ m W (A2)	a= 255.15	[85Vil]
$\alpha$ -Be <sub>3</sub> N <sub>2</sub> (r) T<1450	cI80 Ia $\bar{3}$ Mn <sub>2</sub> O <sub>3</sub> (D $\bar{3}$ )	a= 815.0	[85Vil]; powder pattern: ASTM file card # 4-786 33-192
$\beta$ -Be <sub>3</sub> N <sub>2</sub> (h) T>1450	hP10 P6 <sub>3</sub> /mmc Be <sub>3</sub> N <sub>2</sub>	a= 284.13 c= 969.3	[85Vil]; powder pattern: ASTM file card # 12-649

Tab.2.1 continued

Si	CF8 Fd3m C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160
*BeSiN <sub>2</sub>	oP16 Pna2 <sub>1</sub> MnSiN <sub>2</sub>	a= 497.7 b= 574.7 c= 467.4	[85Vil];powder pattern: ASTM file card # 20-167
*BeSiN <sub>2</sub>	hP4 P6 <sub>3</sub> mc ZnS (B4)	a= 286.9 c= 466.8	[85Vil];powder pattern: ASTM file card # 38-1430
*Be <sub>3</sub> Si <sub>3</sub> N <sub>8</sub>	hR54	a= 286.2 c= 6511	[76Tho];powder pattern: ASTM file card # 32-103
*Be <sub>11</sub> Si <sub>5</sub> N <sub>14</sub>	hR42	a= 286.0 c= 5098	[76Tho];powder pattern: ASTM file card # 32-104
*Be <sub>5</sub> Si <sub>2</sub> N <sub>8</sub>	hP24	a= 286.0 c= 2910	[76Tho];powder pattern: ASTM file card # 32-102
*Be <sub>5</sub> Si <sub>3</sub> N <sub>10</sub>	hR30	a= 285.7 c= 3632	[76Tho];powder pattern: ASTM file card # 32-106
*Be <sub>4</sub> SiN <sub>4</sub>	hP16	a= 286.2 c= 1922	[76Tho];powder pattern: ASTM file card # 32-105
*Be <sub>4</sub> SiN <sub>6</sub>	hR*	a= 286.1 c= 2152	[77Tho];powder pattern: ASTM file card # 33-196

## SYSTEM MAGNESIUM - SILICON - NITROGEN (Mg-Si-N)

### INTRODUCTION / EXPERIMENTAL

One ternary phase is reported to exist in the system Mg-Si-N [72Dav]. The phase was synthesized from  $Mg_3N_2$  (prepared using magnesium (purity: 2N8; from Th. Schuchardt, France) and desoxidized nitrogen) and  $Si_3N_4$  ( $\alpha+\beta$   $Si_3N_4$  containing 0.5 to 2 wt% free silicon; from Th. Schuchardt, France).

### BINARY SYSTEMS

The phase diagram for Mg-Si is given in [86Mas]. No phase diagrams are reported for Mg-N or Si-N.  $Mg_3N_2$  reportedly exists in three modifications  $\alpha$   $^{250^\circ C}$   $\beta$   $^{700^\circ C}$   $\gamma$  [65Ell]. Only the crystal structure for  $\alpha$ - $Mg_3N_2$  is reported (tab.3.1). The melting/dissociation temperature is  $1520^\circ C$  [65Ell].  $Si_3N_4$  exists in two modifications:  $\alpha$ - $Si_3N_4$  and  $\beta$ - $Si_3N_4$  (tab.3.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

Only the section  $Mg_3N_2$ - $Si_3N_4$  of the system Mg-Si-N was investigated. At  $1200^\circ C$  a ternary phase  $MgSiN_2$  (tab.3.1) was observed [72Dav]. At  $1800^\circ C$   $Mg_3N_2$  dissolves 5 mol%  $Si_3N_4$  [85Uch].

### REFERENCES

- [65Ell] R.P. Elliott, "Constitution of Binary Alloys, First Supplement", (McGraw Hill, New York, 1965) p 592
- [72Dav] J. David, "Study on  $Mg_3N_2$  and some of its Compounds", Rev. Chim. Miner. 9 (1972) 717-735
- [76Fro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [85Uch] N. Uchida, M. Koizumi and M. Shimada, "Fabrication of  $Si_3N_4$  Ceramics with Metal Nitride Additives by Isostatic Hot Pressing", J. Amer. Ceram. Soc. 68 (1985) C38-C40
- [85Vil] P. Villars and L.D. Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, OH., 1985)
- [86Mas] T.B. Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer. Soc. Met., Metals Park, OH., 1986)

Table 3.1: Solid phases in the system Mg - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Mg	hP2 P6 <sub>3</sub> /mmc Mg (A3)	a= 320.89 c= 521.01	[85V11]; powder pattern: ASTM file card # 35-821
Mg <sub>2</sub> Si	cF12 Fm $\bar{3}$ m CaF <sub>2</sub> (C1)	a= 633.8	[85V11]; powder pattern: ASTM file card # 35-773
$\alpha$ -Mg <sub>3</sub> N <sub>2</sub> T<550	cI80 Ia $\bar{3}$ Mn <sub>2</sub> O <sub>3</sub> (D5 <sub>2</sub> )	a= 996.4	[85V11]; powder pattern: ASTM file card # 35-778
Si	cF8 Fd $\bar{3}$ m C (A4)	a= 542.86	[85V11]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85V11]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85V11]; powder pattern: ASTM file card # 29-1132 33-1160
*MgSiN <sub>2</sub>	oP16 Pna2 <sub>1</sub> MnSiN <sub>2</sub>	a= 527.9 b= 647.6 c0 499.2	[85V11]; powder pattern: ASTM file card # 25-530

## SYSTEM CALCIUM - SILICON - NITROGEN (Ca-Si-N)

### INTRODUCTION / EXPERIMENTAL

Three ternary phases are reported to exist in the system Ca-Si-N [66-1Lau],[66-2Lau],[68Lau]. The specimens were synthesized from  $\text{Ca}_3\text{N}_2$  (prepared from calcium (from Planet, France) purified by vacuum distillation and desoxidized nitrogen) and  $\text{Si}_3\text{N}_4$  ( $\alpha+\beta$   $\text{Si}_3\text{N}_4$ ; from Th. Schuchardt, France) by heat treatment under nitrogen at  $T \leq 1180^\circ\text{C}$ .

### BINARY SYSTEMS

Phase diagrams for the systems Ca-Si and Ca-N are given in [86Mas]. Additional phases (tab.4.19) are reported for both systems. No phase diagram is reported for Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha$ - $\text{Si}_3\text{N}_4$  and  $\beta$ - $\text{Si}_3\text{N}_4$  (tab.4.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

Only the section  $\text{Ca}_3\text{N}_2$ - $\text{Si}_3\text{N}_4$  of the system Ca-Si-N was investigated [66-1Lau],[66-2Lau],[68Lau]. At  $1180^\circ\text{C}$  the sequence of coexisting phases is  $\text{Si}_3\text{N}_4$ - $\text{CaSiN}_2$ - $\text{Ca}_3\text{Si}_2\text{N}_6$ - $\text{Ca}_2\text{SiN}_4$ - $\text{Ca}_3\text{N}_2$  [68Lau]. The crystal structures of these phases were not determined (tab.4.1). At  $1050^\circ\text{C}$   $\beta$ - $\text{Ca}_3\text{N}_2$  dissolves 1 mol %  $\text{Si}_3\text{N}_4$  [66-2Lau][68Lau].

### REFERENCES

- [66-1Lau] Y. Laurent and J. Lang, "On the Compounds of Silicon Nitride with Calcium Nitride", *Compt. Rend. Acad. Sci. Paris*, C262 (1966) 103-106
- [66-2Lau] Y. Laurent and J. Lang, "Study of the  $\text{Ca}_3\text{N}_2$  Rich Phases in the Binary  $\text{Ca}_3\text{N}_2$ - $\text{Si}_3\text{N}_4$ ", *Compt. Rend. Acad. Sci. Paris*, C263 (1966) 340-343
- [68Lau] Y. Laurent, "Contribution to the Study of the Systems Calcium-Nitrogen and Calcium-Silicon-Nitrogen", *Rev. Chim. Miner.* 5 (1968) 1019-1050
- [76Fro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)

[85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)

[86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)

Table 4.1: Solid phases in the system Ca - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\alpha$ -Ca(r) T<443	cF4 Fm $\bar{3}$ m Cu (A1)	a= 558.84	[85Vil]; powder pattern: ASTM file card # 23-430
$\beta$ -Ca(h) T>443	cI2 Im $\bar{3}$ m W (A2)	a= 448.0	[85Vil]; powder pattern: ASTM file card # 10-348
Ca <sub>2</sub> Si	oP12 Pnma Cq <sub>2</sub> Si (C23)	a= 766.7 b= 479.9 c= 900.2	[85Vil]; powder pattern: ASTM file card # 28-235
Ca <sub>3</sub> Si <sub>2</sub>	tI32 I4/mcm Cr <sub>2</sub> B <sub>2</sub> (D8 <sub>1</sub> )	a= 764 c= 1462	[85Vil] note: not incl. in the phase diagram
CaSi	oC8 Cmcm CrB (B33)	a= 454.5 b= 1072.8 c= 389.0	[85Vil]; powder pattern: ASTM file card # 26-324
CaSi <sub>2</sub>	hR6 R $\bar{3}$ m CaSi <sub>2</sub> (C12)	a= 385.5 c= 3060	[85Vil]; powder pattern: ASTM file card # 1-1276



Tab.4.1 continued

$\text{Ca}_2\text{N}$	hR3	a= 363.8	[85V11]; powder pattern:
	$\text{R}\bar{3}\text{m}$	c= 1878	ASTM file card # 21-837
	Sm (C19)		
or:	m**	a= 753.5	[68Lau]
		b= 363.8	
		c= 629.9	
		$\beta = 123.85^\circ$	
$\alpha\text{-Ca}_3\text{N}_2$	cI80	a= 1147.3	[85V11]; powder pattern:
	$\text{Ia}\bar{3}$		ASTM file card # 22-152
	$\text{Mn}_2\text{O}_3$ (D5 <sub>3</sub> )		
$\gamma\text{-Ca}_3\text{N}_2$	o*40	a= 1782	[85V11]; powder pattern:
		b= 1156	ASTM file card # 21-153
		c= 358	
$\text{Ca}_4\text{N}_6$	tP38	a= 1445	[85V11]; powder pattern:
	$\text{P4}_2/\text{mm}$	c= 360	ASTM file card # 22-151
	$\text{Ca}_4\text{N}_6$		
$\text{CaN}_2$	oF56	a= 1132	[85V11]; powder pattern:
	Fddd	b= 1107	ASTM file card # 21-832
		c= 595	
Si	cF8	a= 542.86	[85V11]; powder pattern:
	$\text{Fd}\bar{3}\text{m}$		ASTM file card # 5-565
	C (A4)		
$\alpha\text{-Si}_3\text{N}_4$	hP28	a= 781.8	[85V11]; powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	$\text{Si}_3\text{N}_4$		
$\beta\text{-Si}_3\text{N}_4$	hP14	a= 760.8	[85V11]; powder pattern:
	$\text{P6}_3/\text{m}$	c= 291.1	ASTM file card # 29-1132
	$\text{Si}_3\text{N}_4$		33-1160
* $\text{CaSiN}_2$			[68Lau]; powder pattern:
			ASTM file card # 20-230
* $\text{Ca}_2\text{SiN}_4$			[68Lau]; powder pattern:
			ASTM file card # 21-162
* $\text{Ca}_3\text{Si}_2\text{N}_6$			[68Lau]; powder pattern:
			ASTM file card # 21-160

## SYSTEM STRONTIUM - SILICON - NITROGEN (Sr-Si-N)

### INTRODUCTION / EXPERIMENTAL

Two ternary phases are reported to exist in the system Sr-Si-N [69Gau]. The samples were synthesized from  $\text{Sr}_3\text{N}_2$  (prepared from strontium purified by vacuum distillation and desoxidized nitrogen) and  $\text{Si}_3\text{N}_4$  ( $\alpha$ - $\beta$   $\text{Si}_3\text{N}_4$ , from Th. Schuchardt, France) by heat treatment under nitrogen at 960°C.

### BINARY SYSTEMS

A phase diagram for the system Sr-Si is given in [86Mas]. In addition the phases  $\text{Sr}_2\text{Si}$  and  $\text{Sr}_5\text{Si}_3$  are reported (tab.5.1). No phase diagrams are reported for Sr-N or Si-N. In the Sr-N system a phase ranging in composition from  $\text{SrN}_{0.5}$  to  $\text{SrN}_{0.67}$  as well as the azide  $\text{SrN}_3$  are structurally characterized (tab.5.1).  $\text{Sr}_3\text{N}_2$  melts at 1030°C [65Ell].  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha$ - $\text{Si}_3\text{N}_4$  and  $\beta$ - $\text{Si}_3\text{N}_4$  (tab.5.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

Only the section  $\text{Sr}_3\text{N}_2$ - $\text{Si}_3\text{N}_4$  of the system Sr-Si-N was investigated [69Gau]. At 960°C the sequence of coexisting phases is  $\text{Si}_3\text{N}_4$ - $\text{SrSiN}_2$ - $\text{Sr}_4\text{SiN}_4$ - $\text{Sr}_3\text{N}_2$  [69Gau]. The crystal structures of these phases were not determined (tab.5.1).

### REFERENCES

- [65Ell] R.P. Elliott, "Constitution of Binary Alloys, First Supplement", (McGraw Hill, New York, 1965)
- [69Gau] J. Gaude and J. Lang, "On the System  $\text{Si}_3\text{N}_4$ - $\text{Sr}_3\text{N}_2$ ", Compt. Rend. Acad. Sci. Paris C268 (1969) 1785-1788
- [70Gau] J. Gaude and J. Lang, "The System Strontium-Nitrogen", Rev. Chim. Miner. 7 (1970) 1059-1067
- [76Fro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [85Vil] P. Villars and L.D. Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, OH., 1985)
- [86Mas] T.B. Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer. Soc. Met., Metals Park, OH., 1986)

Table 5.1: Solid phases in the system Sr - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\alpha$ -Sr(r) T<547	cF4 Fm $\bar{3}$ m Cu (A1)	a= 608.4	[85Vil]; powder pattern: ASTM file card # 15-305
$\beta$ -Sr(h) T>547	cI2 Im $\bar{3}$ m W (A2)	a= 487	[86Mas]; powder pattern: ASTM file card # 15-288
Sr <sub>2</sub> Si	oP12 Pnma C <sub>2</sub> Si (C23)	a= 811 b= 515 c= 954	[85Vil] note: not. incl. in the phase diagram; powder pattern: ASTM file card # 30-1303
Sr <sub>5</sub> Si <sub>3</sub>	tI32 I4cm Sr <sub>5</sub> Si <sub>3</sub>	a= 805.5 c= 1568.8	[85Vil] note: not incl. in the phase diagram
SrSi	oC8 Cmcm CrB (B33)	a= 482.6 b= 1128.7 c= 404.2	[85Vil]; powder pattern: ASTM file card # 16-8
SrSi <sub>2</sub>	cP12 P4 <sub>3</sub> <sup>32</sup> SrSi <sub>2</sub>	a= 654.0	[85Vil]; powder pattern: ASTM file card # 38-1366
Sr <sub>2</sub> N	hR3 R $\bar{3}$ m Sm (C19)	a= 724.6 $\alpha$ = 30.8°	[85Vil]; powder pattern: ASTM file card # 27-855
or:	m**	a= 719 b= 385 c= 665 $\beta$ = 108°	[70Gau]
Sr <sub>3</sub> N <sub>2</sub>	hP*		
	Ba <sub>3</sub> N <sub>2</sub>		

Tab.5.1 continued

$\text{SrN}_2$	oF56 Fddd	a= 1180.88 b= 1153.43 c= 611.62	[85Vil]; powder pattern: ASTM file card # 21-1466
Si	cF8 Fd $\bar{3}$ m C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha\text{-Si}_3\text{N}_4$	hP28 P31c	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta\text{-Si}_3\text{N}_4$	$\text{Si}_3\text{N}_4$ hP14 P6 $_3$ /m $\text{Si}_3\text{N}_4$	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160
* $\text{SrSiN}_2$			[69Gau]; powder pattern: ASTM file card # 22-1438
* $\text{Sr}_2\text{SiN}_4$			[69Gau]; powder pattern: ASTM file card # 22-1439

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## SYSTEM BARIUM - SILICON - NITROGEN (Ba-Si-N)

### INTRODUCTION / EXPERIMENTAL

One ternary phase is reported to exist in the system Ba-Si-N [72Gau],[84Mor]. The samples were synthesized from  $Ba_3N_2$  and  $Si_3N_4$  by heat treating under nitrogen at 1000°C [72Gau] or 1500°C [84Mor].

### BINARY SYSTEMS

For the system Ba-Si a phase diagram is given in [86Mas]. Several additional phases are reported to exist (tab.6.1). No phase diagrams are reported for Ba-N or Si-N. The nitride  $Ba_3N_2$  and the azide  $BaN_3$  are structurally characterized (tab.6.1).  $Si_3N_4$  exists in two modifications:  $\alpha$ - $Si_3N_4$  and  $\beta$ - $Si_3N_4$  (tab.6.1). The solubility of nitrogen in silicon is very low [76Pro].

### SOLID PHASES / ISOTHERMAL SECTIONS

The section  $Ba_3N_2$ - $Si_3N_4$  of the system Ba-Si-N was investigated [72Gau][84Mor]. The only ternary phase observed is  $BaSiN_2$  (tab.6.1).

### REFERENCES

- [72Gau] J.Gaude and J.Lang, "On the Preparation of  $Ba_3N_2$  and a Phase of the Type  $BaSiN_2$ ", Compt.Rend.Acad.Sci.Paris C274 (1972) 521-523
- [76Pro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [84Mor] P.E.D.Morgan, "X-Ray Powder Diffraction Pattern and Unit Cell of  $BaSiN_2$ ", J.Mater.Sci.Lett. 3 (1984) 131-132
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)

Table 6.1: Solid phases in the system Ba - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Ba	cI2 Im $\bar{3}$ m W (A2)	a= 501.3	[85Vil]; powder pattern: ASTM file card # 6-235
Ba <sub>2</sub> Si	oP12 Pnma C <sub>2</sub> Si (C23)	a= 843 b= 540 c= 988	[85Vil]; powder pattern ASTM file card # 30-154 note: not included in the phase diagram
Ba <sub>3</sub> Si <sub>3</sub>	tP32 P4/ncc Ba <sub>3</sub> Si <sub>3</sub>	a= 843.6 c= 1653.5	[85Vil]; powder pattern: ASTM file card # 27-187 note: not included in the phase diagram
BaSi	oC8 Cmcm CrB (B33)	a= 504.2 b= 1197 c= 414.2	[85Vil]; powder pattern: ASTM file card # 19-135
Ba <sub>3</sub> Si <sub>4</sub>	tP28 P4 <sub>2</sub> /mmn Ba <sub>3</sub> Si <sub>4</sub>	a= 852 c= 1184	[85Vil] note: not incl. in the phase diagram
BaSi <sub>2</sub>	hP3 P6/mmm AlB <sub>2</sub> (C32)	a= 439 c= 483	[85Vil];
BaSi <sub>2</sub>	oP24 Pnma BaSi <sub>2</sub>	a= 892 b= 680 c= 1158	[85Vil]; powder pattern: ASTM file card # 31-163
Ba <sub>3</sub> N <sub>2</sub> (Ba <sub>3</sub> N <sub>4</sub> )	hP* Ba <sub>3</sub> N <sub>2</sub>	a= 522 c= 550	[85Vil]; powder pattern: ASTM file card # 27-39
BaN <sub>2</sub>	mP14 P2 <sub>1</sub> /m BaN <sub>2</sub>	a= 959 b= 439 c= 542 $\beta$ = 99.7°	[85Vil]; powder pattern: ASTM file card # 18-154

Tab.6.1 cont.

Si	CF8 Fd3m C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160
*BaSiN <sub>2</sub>	O**	a= 559 b= 754.2 c= 1134.0	[84Mor];powder pattern: ASTM file card # 36-1257

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## SYSTEM SCANDIUM - SILICON - NITROGEN (Sc-Si-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria of Sc-Si-N at 800°C and 1000°C were determined by x-ray analysis [90Wei]. The alloys were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si), silicon (purity: 3N) both from Alpha Div., Ventron Corp., USA and scandium (purity 4N; from Rare Earth Products Ltd., UK). Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were sealed in evacuated quartz tubes lined with Mo foil and heat treated for 340h at 800°C or 170h at 1000°C.

### BINARY SYSTEMS

The phase diagram for Sc-Si due to [86Gok] is reproduced in [76Mof]. The intermediate phases are described in tab.7.1. The decomposition of the phase  $\text{ScSi}_{2-x}$  ( $\text{Sc}_x\text{Si}_2$ ) into  $\text{ScSi} + \text{Si}$  is observed at temperatures below 1000°C [87Sch]. No phase diagrams are reported for Sc-N or Si-N. At normal pressure ScN is the only stable scandium nitride [72Kie].  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.7.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in the system Sc-Si-N (tab.7.1). ScN dominates the isothermal section at 800°C (fig.7.1 [90Wei]): It coexists with all phases stable at this temperature. At 1000°C (fig.7.2 [90Wei]) ScN coexists with all three binary scandium silicides but not with silicon. Thus,  $\text{Si}_3\text{N}_4$  in contact with scandium is decomposed at elevated temperatures.



## REFERENCES

- [72Kie] R.Kieffer, P.Ettmayer and S.Pajakoff, "On the Mononitrides and on Nitrogen Rich Nitrides of the Rare Earth, I Comm.", *Monatsh. Chem.* 103 (1972) 1285-1298
- [76Pro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [76Mof] W.Moffatt, "The Handbook of Binary Phase Diagrams", (General Electric Comp., Schenectady, NY, 1976 and updates)
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Gok] A.B.Gokhale and G.J.Abbaschian, "The Sc-Si (Scandium-Nitrogen) System", *Bull.Alloy Phase Diagr.* 7 (1986) 333-336
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [87Sch] J.C.Schuster in "Boron Nitride and Silicon Nitride Systems", Report to the USA European Research Office under Contract DAJA45-84-C-0038 (1987)
- [90Wei] F.Weitzer, J.C.Schuster, J.Bauer and B.Jounel, "Phase Equilibria in Ternary RE-Si-N Systems (RE= Sc, Ce, Ho)", *J.Mater.Sci.* 25 (1990)

Table 7.1: Solid phases in the system Sc - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\alpha$ -Sc(r) T<1337	hP2 P6 <sub>3</sub> /mmc Mg (A3)	a= 330.8 c= 526.7	[85Vil]; powder pattern: ASTM file card # 17-714
$\beta$ -Sc(h) T>1337	cI2 Im $\bar{3}$ m W (A2)	a= 454.1	[86Mas]
Sc <sub>3</sub> Si <sub>2</sub>	hP16 P6 <sub>3</sub> /mcm Mn <sub>3</sub> Si <sub>2</sub> (D8 <sub>h</sub> )	a= 786.1 c= 581.2	[85Vil]; powder pattern: ASTM file card #15-189
ScSi	oC8 Cmcm CrB (B33)	a= 398.8 b= 988.2 c= 365.9	[85Vil]; powder pattern: ASTM file card # 18-1161
ScSi <sub>1-x</sub> (Sc <sub>3</sub> Si <sub>2</sub> ) T>800	hP3 P6/mmm AlB <sub>2</sub> (C32)	a= 366 c= 387	[85Vil]; powder pattern: ASTM file card # 17-93
ScN	cF8 Fm $\bar{3}$ m NaCl (B1)	a= 450.5	[85Vil]; powder pattern: ASTM file card # 3-951, 31-1493, 35-753
Si	cF8 Fd $\bar{3}$ m C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160

Fig.7.1: Isothermal section observed in the system Sc - Si - N  
at 800°C (in the absence of external nitrogen pressure)

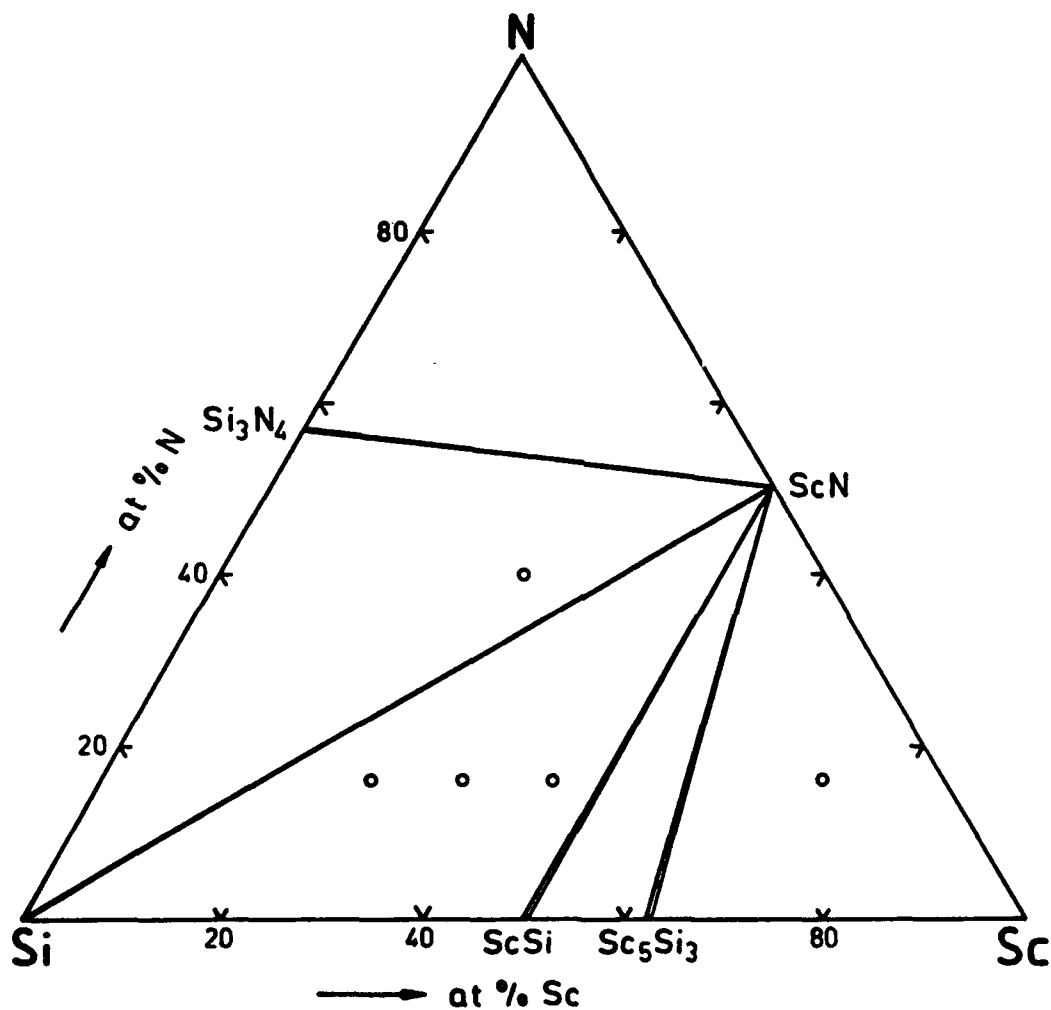
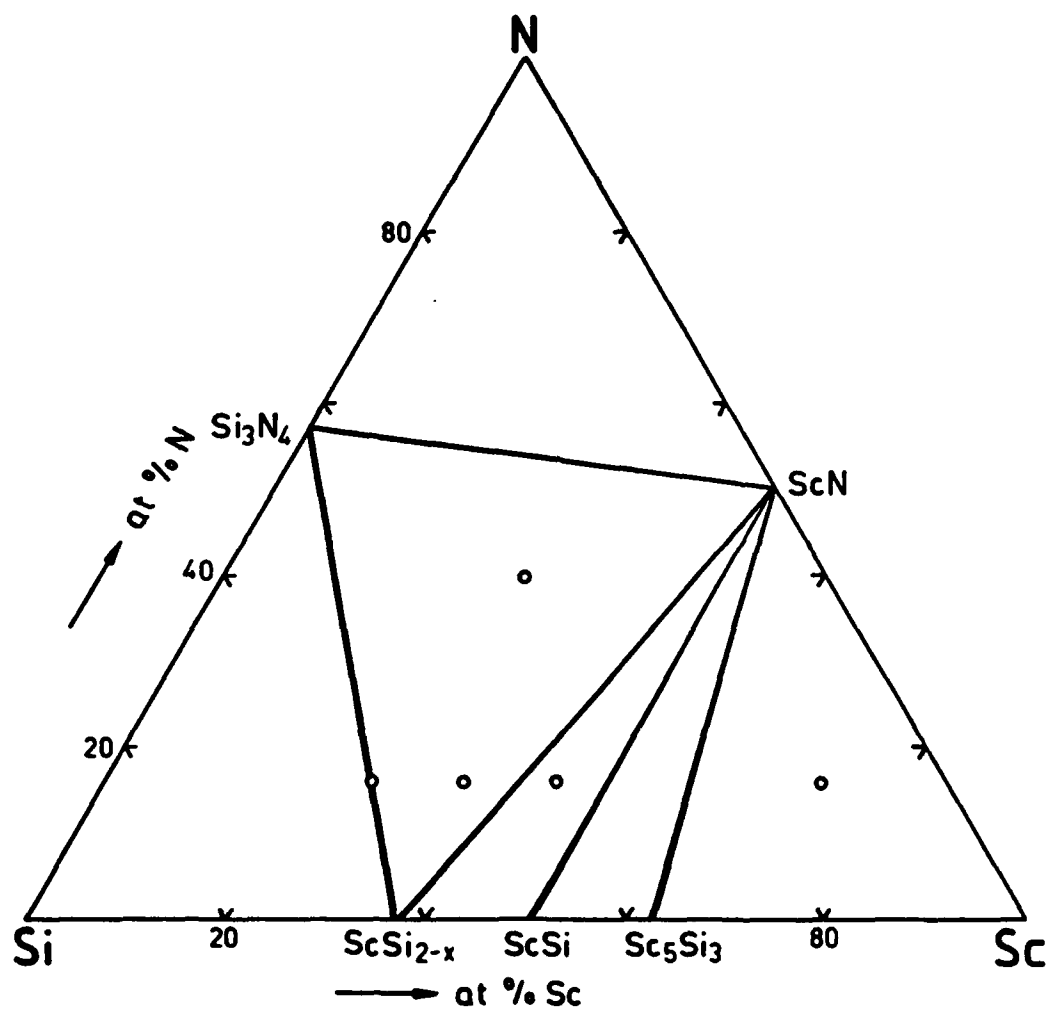


Fig.7.2: Isothermal section observed in the system Sc - Si - N  
at 1000°C (in the absence of external nitrogen pressure)



## **SYSTEM YTTRIUM - SILICON - NITROGEN (Y-Si-N)**

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### **INTRODUCTION / EXPERIMENTAL**

Three ternary phases are reported to exist at 1700°C in the system Y-Si-N [86Jac]. No experimental details are given.

### **BINARY SYSTEMS**

The phase diagram for Y-Si is given in [86Mas] and was thermodynamically modelled by [89Ran]. The intermediate phases are described in tab.8.1. A tentative phase diagram for Y-N was proposed by [74Car] and is reproduced in [76Mof]. No phase diagram is reported for Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.8.1). The solubility of nitrogen in silicon is very low [76Fro].

### **SOLID PHASES / ISOTHERMAL SECTIONS**

Only the section YN- $\text{Si}_3\text{N}_4$  of the system Y-Si-N was investigated [85Uch][86Jac]. At 1700°C the sequence of coexisting phases is  $\text{Si}_3\text{N}_4$  -  $\text{YSi}_3\text{N}_7$  -  $\text{Y}_2\text{Si}_2\text{N}_6$  -  $\text{Y}_6\text{Si}_3\text{N}_{10}$  - YN [86Jac]. The crystal structures of these phases were not reported.  $\text{Si}_3\text{N}_4$  dissolves 3 mol% YN at 1650°C and 5 mol% YN at 1800°C [85Uch]. Using the thermochemical data given in tab.8.2 an isothermal section for 1000°C is calculated (fig.8.1) showing, that  $\text{Si}_3\text{N}_4$  does not coexist with yttrium at high temperatures.

## REFERENCES

- [74Car] O.N. Carlson, R.R. Lichtenberg and J.C. Warner, "Solid Solubilities of Oxygen, Carbon and Nitrogen in Yttrium", *J. Less Common Metals* 35 (1974) 275-284
- [76Mof] W. Moffatt, "The Handbook of Binary Phase Diagrams", (General Electric Comp., Schenectady, NY, 1976 and updates)
- [76Fro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [78Fro] E. Fromm, H. Jehn and G. Hörz, "Gases and Carbon in Metals", *ZAED, Physics Data* 5-3 (1978) pp2
- [85Uch] N. Uchida, M. Koizumi and M. Shimada, "Fabrication of Si<sub>3</sub>N<sub>4</sub> Ceramics with Metal Nitride Additives by Isostatic Hot Pressing", *J. Amer. Ceram. Soc.* 68 (1985) C38-C40
- [85Vil] P. Villars and L.D. Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, OH., 1985)
- [86Jac] K.H. Jack, "Sialons: A Study in Materials Development", in "Non Oxide Technical and Engineering Ceramics", S. Hampshire (ed.) (Elsevier, London, UK, 1986) 1-30
- [86Mas] T.B. Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer. Soc. Met., Metals Park, OH., 1986)
- [89Ran] Q. Ran, H.L. Lukas, G. Effenberg and G. Petzow, "A Thermodynamic Assessment of the Y-Si System", *Z. Metalk.* 80 (1989) 402-405

Table 8.1: Solid phases in the system Y - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\alpha$ -Y(r) T<1478	hP2 P6 <sub>3</sub> /mmc Mg (A3)	a= 365.09 c= 573.88	[85Vil]; powder pattern: ASTM file card # 33-1458
$\beta$ -Y (h) T>1478	cI2 Im $\bar{3}$ m W (A2)	c= (407)	[86Mas]
Y <sub>2</sub> Si <sub>3</sub>	hP16 P6 <sub>3</sub> /mmc Mn <sub>2</sub> Si <sub>3</sub> (D8 <sub>8</sub> )	a= 840.3 c= 630.3	[85Vil]; powder pattern: ASTM file card # 24-1026
Y <sub>3</sub> Si <sub>4</sub>	oP36 Pnma Sn <sub>3</sub> Ge <sub>4</sub>	a= 739 b= 1452 c= 764	[85Vil]
YSi	oC8 Cmcm CrB (B33)	a= 425.1 b= 1052.6 c= 382.6	[85Vil]; powder pattern: ASTM file card # 12-620
YSi <sub>2-x</sub> (Y <sub>2</sub> Si <sub>3</sub> )	hP3 P6/mmm AlB <sub>2</sub> (C32)	a= 384.2 c= 414.0	[85Vil]; powder pattern: ASTM file card # 11-596
YSi <sub>2</sub> (r) T<1250	oI12 Imma GdSi <sub>2</sub>	a= 405 b= 395 c= 1322	[85Vil]; powder pattern: ASTM file card # 11-324
YSi <sub>2</sub> (h) (Y <sub>2</sub> Si <sub>3</sub> ) T>1250	tI12 I4 <sub>1</sub> /amd ThSi <sub>2</sub> (C <sub>c</sub> )	a= 404 c= 1342	[85Vil]
YN	cF8 Fm $\bar{3}$ m NaCl (B1)	a= 488.9	[85Vil]; powder pattern: ASTM file card # 10-221 35-779
Si	cF8 Fd $\bar{3}$ m C (A4)	a= 357.0 c= 357.0	[85Vil]; powder pattern: ASTM file card # 5-565

Tab.8.1 continued

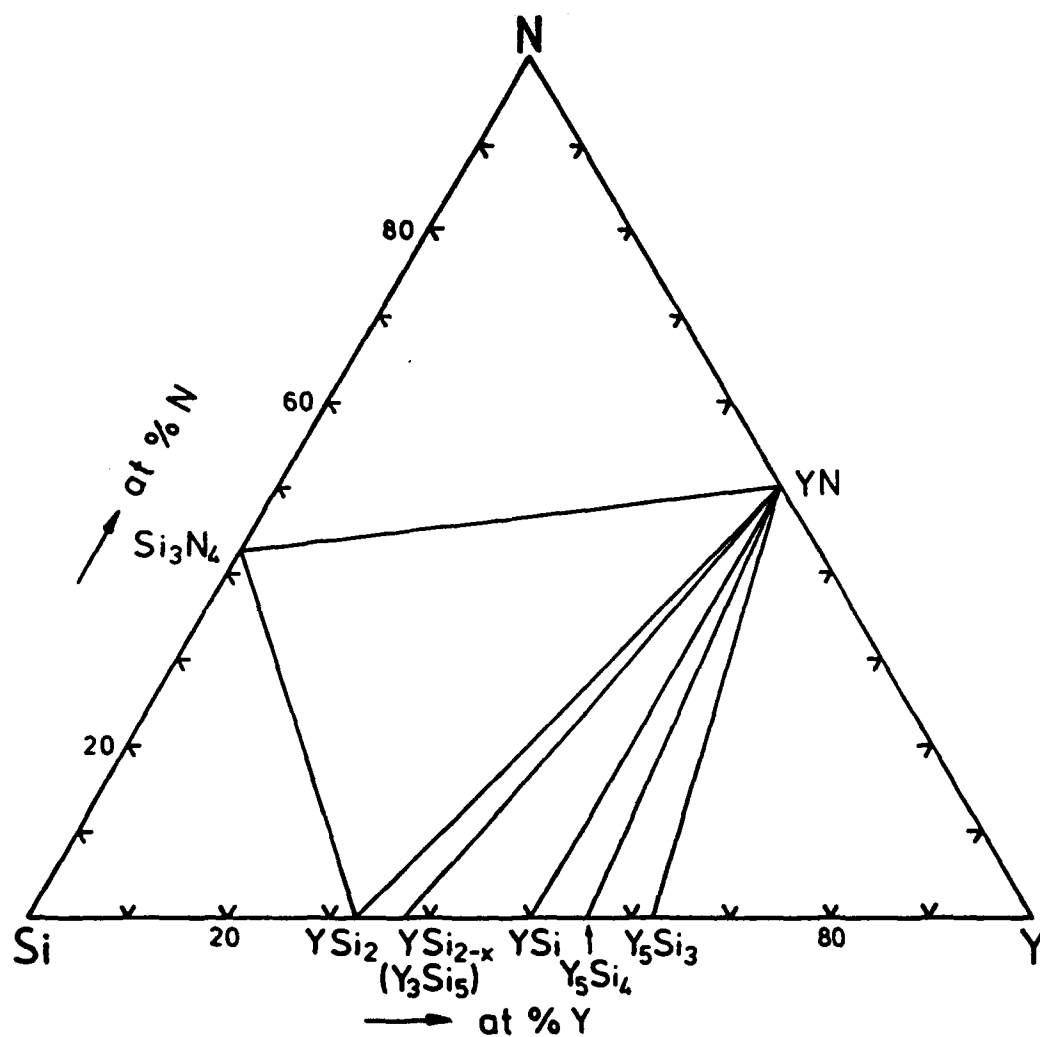
$\alpha$ - $\text{Si}_3\text{N}_4$	hP28	a= 781.8	[85Vil]; powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	$\text{Si}_3\text{N}_4$		
$\beta$ - $\text{Si}_3\text{N}_4$	hP14	a= 760.8	[85Vil]; powder pattern:
	P6 <sub>3</sub> /m	c= 291.1	ASTM file card # 29-1132
	$\text{Si}_3\text{N}_4$		33-1160
$*\text{Y}_6\text{Si}_3\text{N}_{10}$			[86Jac]
$*\text{Y}_2\text{Si}_3\text{N}_6$			[86Jac]
$*\text{YSi}_3\text{N}_5$			[86Jac]

Tab.8.2: Thermodynamic data for the solid phases in Y - Si - N

phase	$\Delta G_f^\circ$ (J/gramatom)	Comment
.1429 $\text{Si}_3\text{N}_4$	-124602 + 57.95 T	[76Fro]
.3333 $\text{YSi}_2$	-38921 + 2.500 T	[89Ran]
.1250 $\text{Y}_3\text{Si}_5$	-44430 + 4.0 T	[89Ran]
.5000 $\text{YSi}$	-61920 + 10.665 T	[89Ran]
.1111 $\text{Y}_3\text{Si}_4$	-65150 + 12.60 T	[89Ran]
.1250 $\text{Y}_2\text{Si}_3$	-60000 + 11.187 T	[89Ran]
.5000 $\text{YN}$	-149490 + 41.72 T	(289 1134K) [78Fro]
	-152415 + 44.32 T	(1134-1193K) [78Fro]
	-154515 + 46.105 T	(1193-2273K) [78Fro]



**Fig.8.1: Isothermal section calculated for the system Y - Si - N  
at 1000°C (ignoring the possible existence of ternary phases)**



## SYSTEM LANTHANUM - SILICON - NITROGEN (La-Si-N)

### INTRODUCTION / EXPERIMENTAL

One ternary phase is reported in the system La-Si-N [80Ino][81Hol]. In the latter work samples were prepared by hot pressing from LaN and  $\text{Si}_3\text{N}_4$  at 1800°C.

### BINARY SYSTEMS

No phase diagrams are reported for any of the binary boundary systems. Six intermediate lanthanum silicides are known (tab.9.1). The phase LaN is under normal pressure the only stable lanthanum nitride [72Kie].  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.9.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

The ternary phase  $\text{LaSi}_3\text{N}_5$  [80Ino][81hol]] is described in tab.9.1.

### REFERENCES

- [72Kie] R.Kieffer, P.Ettmayer and S.Pajakoff, "On the Mononitrides and on Nitrogen Rich Nitrides of the Rare Earth, 1<sup>st</sup> Comm.", *Monatsh. Chem.* 103 (1972) 1285-1298
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [80Ino] Z.Inoue, M.Mitomo and N.Ii, "A Crystallographic Study of a New Compound of Lanthanum Silicon Nitride  $\text{LaSi}_3\text{N}_5$ ", *J.Mater.Sci.* 15 (1980) 2915-2920
- [81Hol] C.E.Holcombe and L.Kovach, "Advanced Ceramic Materials for Hydrogen-Fluorine Environments", *Ceram.Bull.* 60 (1981) 546-548
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)

Table 9.1: Solid phases in the system La - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\alpha$ -La(r) T<310	hP4 P6 <sub>3</sub> /mmc La (A3')	a= 377 c= 1215.9	[85V11]; powder pattern: ASTM file card # 2-618
$\beta$ -La(h) 310<T<865	cF4 Fm $\bar{3}$ m Cu (A1)	a= 529.1	[85V11]; powder pattern: ASTM file card # 2-607
$\gamma$ -La(h) T>865	cI2 Im $\bar{3}$ m W (A2)	a= 426	[85V11]
La <sub>3</sub> Si <sub>3</sub>	tI32 I4/mcm Cr <sub>2</sub> B <sub>2</sub> (D8 <sub>1</sub> )	a= 795.3 c= 1404	[85V11]; powder pattern: ASTM file card # 20-555
La <sub>3</sub> Si <sub>2</sub>	tP10 P4/nbm U <sub>3</sub> Si <sub>2</sub> (D5 <sub>a</sub> )	a= 787 c= 450	[85V11]; powder pattern: ASTM file card # 19-660
La <sub>3</sub> Si <sub>4</sub>	tP36 P4 <sub>1</sub> 2 <sub>1</sub> 2 Zr <sub>3</sub> Si <sub>4</sub>	a= 804 b= 1543	[85V11]
LaSi	oP8 Pnma FeB (B27)	a= 838 b= 399 c= 602	[85V11]; powder pattern: ASTM file card # 19-661
LaSi <sub>2</sub> (r)	oI12 Imma GdSi <sub>2</sub>	a= 427.0 b= 417.0 c= 1405	[85V11]; powder pattern: ASTM file card # 20-553
LaSi <sub>2</sub> (h)	tI12 I4 <sub>1</sub> /amd ThSi <sub>2</sub> (C <sub>c</sub> )	a= 432.2 c= 1386	[85V11]; powder pattern: ASTM file card # 6-471
LaN	cF8 Fm $\bar{3}$ m NaCl (B1)	a= 530.5	[85V11]; powder pattern: ASTM file card # 15-892

Tab.9.1 continued

Si	CF8 Fd $\bar{3}m$ C (A4)	a= 542.86	[85V11]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85V11]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85V11]; powder pattern: ASTM file card # 29-1132 33-1160
*LaSi <sub>3</sub> N <sub>5</sub>	oP36 P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> LaSi <sub>3</sub> N <sub>5</sub>	a= 783.8 b= 1123.6 c= 480.7	[85V11]; powder pattern: given in [80Ino]

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## **SYSTEM CERIUM - SILICON - NITROGEN (Ce-Si-N)**

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### **INTRODUCTION / EXPERIMENTAL**

Phase equilibria of Ce-Si-N at 1000°C were determined by x-ray analysis [90Wei]. The alloys were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si), silicon (purity: 3N) both from Alpha Div., Ventron Corp., USA and cerium (purity 3N; from Rare Earth Products Ltd., UK). Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were sealed in evacuated quartz tubes lined with Mo foil and heat treated for 240h at 1000°C.

### **BINARY SYSTEMS**

The phase diagram for Ce-Si (fig.10.1) was assessed in [89Mun]. The intermediate phases are described in tab.10.1. A tentative phase diagram for Ce-N is given in [86Mas]. No phase diagram is reported for Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.10.1). The solubility of nitrogen in silicon is very low [76Pro].

### **SOLID PHASES / ISOTHERMAL SECTIONS**

No ternary phase exists in the system Ce-Si-N (tab.10.1). The isothermal section at 1000°C (fig.10.2 [90Wei]) shows CeN to coexist with all six binary cerium silicides as well as silicon nitride but not with silicon. Thus,  $\text{Si}_3\text{N}_4$  in contact with cerium is decomposed at elevated temperatures.

## REFERENCES

- [76Pro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [82Yas] H. Yashima and T. Sato, "Non Magnetic-Magnetic Transition in Ce-Si System", Solid State Commun. 41 (1982) 723-727
- [85Vil] P. Villars and L. D. Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, OH., 1985)
- [86Mas] T. B. Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer. Soc. Met., Metals Park, OH., 1986)
- [89Mun] A. Munitz, A. B. Gokhale and G. J. Abbaschian, "The Ce-Si (Cerium-Silicon) System", Bull. Alloy Phase Diagr. 10 (1989) 73-78
- [90Wei] F. Weitzer, J. C. Schuster, J. Bauer and B. Jounel, "Phase Equilibria in Ternary Re-Si-N Systems (RE= Sc, Ce, Ho)", J. Mater. Sci. 25 (1990)

Table 10.1: Solid phases in the system Ce - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\beta$ -Ce(r) T<61	bP4 P6 <sub>3</sub> /mmc La (A3')	a= 368.10 c= 1185.7	[85Vil]
$\gamma$ -Ce(h) 61<T<726	cF4 Fm $\bar{3}$ m Cu (A1)	a= 515.58	[85Vil]; powder pattern: ASTM file card # 8-56
$\delta$ -Ce(h) T>726	cI2 Im $\bar{3}$ m W (A2)	a= 412.0	[86Mas]
Ce <sub>3</sub> Si <sub>3</sub>	tI32 I4/mcm Ce <sub>3</sub> B <sub>3</sub> (D8 <sub>1</sub> )	a= 789 c= 1377	[85Vil]; powder pattern: ASTM file card # 19-297
Ce <sub>3</sub> Si <sub>2</sub>	tP10 P4/nbm U <sub>3</sub> Si <sub>2</sub> (D5 <sub>a</sub> )	a= 779 c= 436	[85Vil]
Ce <sub>3</sub> Si <sub>4</sub>	tP36 P4 <sub>1</sub> 2 <sub>1</sub> 2 Zr <sub>3</sub> Si <sub>4</sub>	a= 793 b= 1504	[85Vil]
CeSi	oP8 Pnma FeB (B27)	a= 830.2 b= 396.2 c= 596.4	[85Vil]; powder pattern: ASTM file card # 18-320
CeSi <sub>2-x</sub> (Ce <sub>3</sub> Si <sub>3</sub> )	oI12 Imma GdSi <sub>2</sub>	a= 416.8 b= 409.8 c= 1381.5	[82Yas]
CeSi <sub>2</sub>	tI12 I4 <sub>1</sub> /amd ThSi <sub>2</sub> (C <sub>c</sub> )	a= 418.4 c= 1385.6	[85Vil]; powder pattern: ASTM file card # 6-485
CeN	cF8 Fm $\bar{3}$ m NaCl (B1)	a= 502.45	[85Vil]; powder pattern: ASTM file card # 15-882

Tab.10.1 continued

Si	CF8 Pd5m C (A4)	a= 542.86	[85V11]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85V11]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>2</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85V11]; powder pattern: ASTM file card # 29-1132 33-1160

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Fig.10.1: Phase diagram for the boundary system cerium - silicon

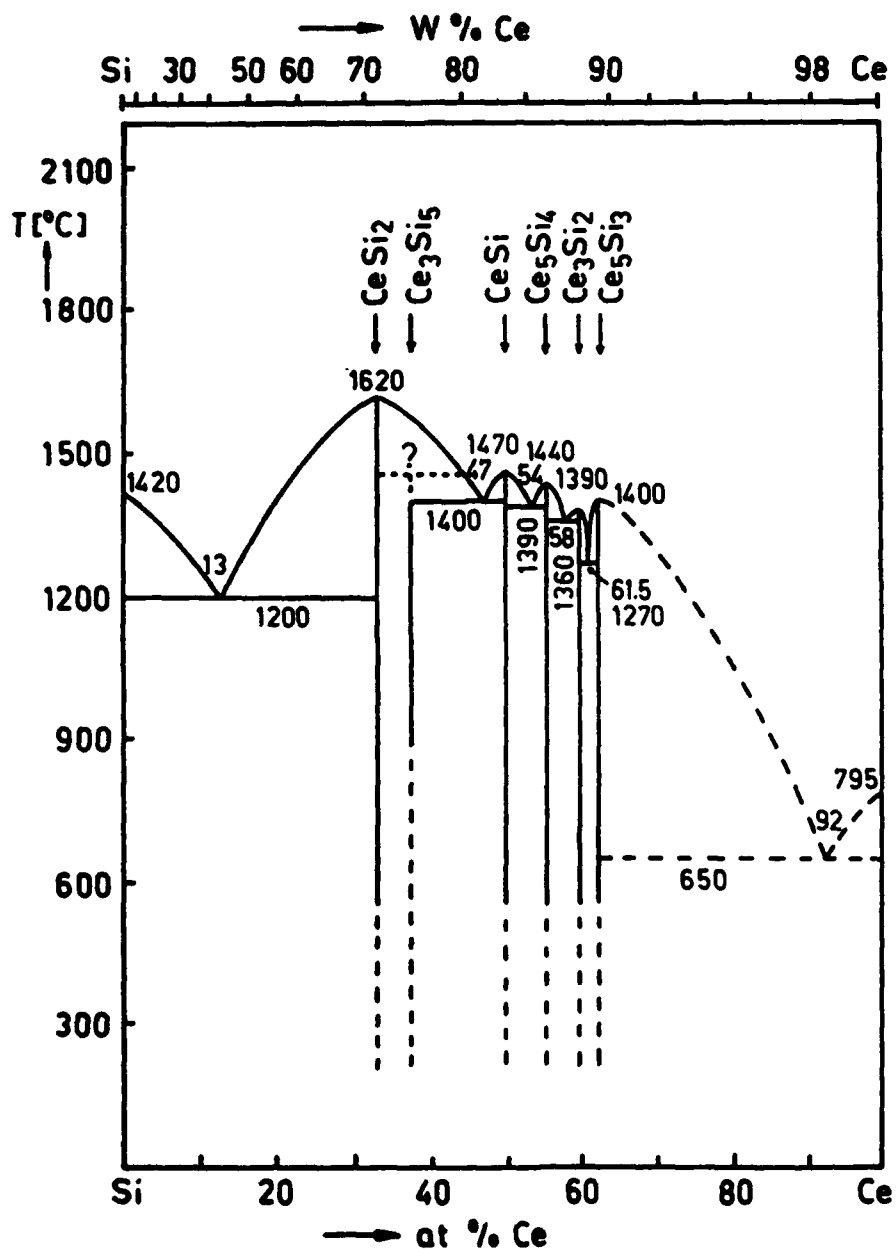
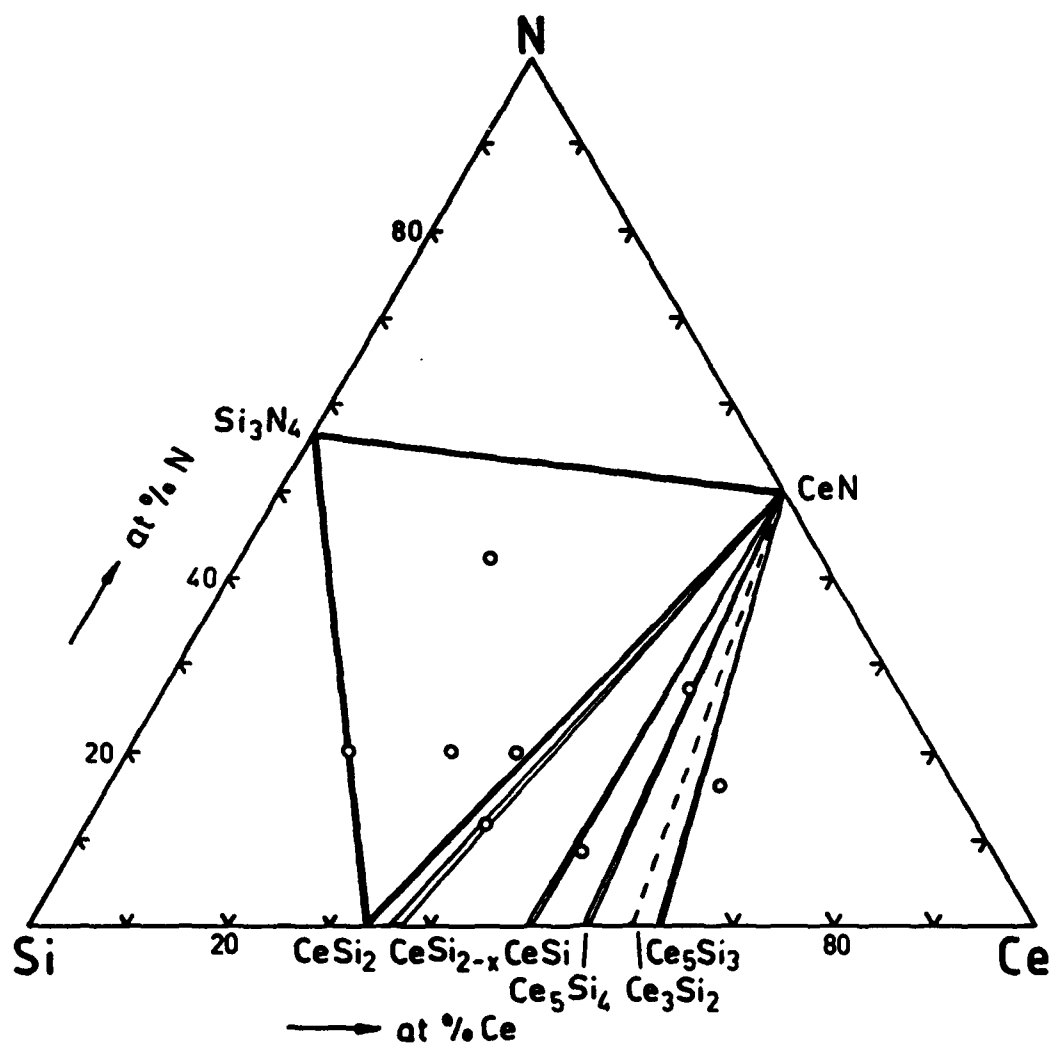


Fig.10.2: Isothermal section observed in the system Ce - Si - N  
at 1000°C (in the absence of external nitrogen pressure)



## **SYSTEM SAMARIUM - SILICON - NITROGEN (Sm-Si-N)**

### **INTRODUCTION / EXPERIMENTAL**

The ternary phase  $\text{Sm}_2\text{Si}_2\text{N}_4$  is reported [83Gau]. The sample was synthesized from SmN (prepared by reacting samarium with nitrogen) and  $\text{Si}_3\text{N}_4$  ( $\alpha+\beta$   $\text{Si}_3\text{N}_4$ , from E. Merck, FRG) by heat treatment at 1200°C under nitrogen.

### **BINARY SYSTEMS**

The phase diagram for the binary Sm-Si (fig.11.1) assessed by [88Gok]. The intermediate phases are described in tab.11.1. No phase diagrams are reported for Sm-N or Si-N. SmN is the only samarium nitride reported [72Kie].  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha$ - $\text{Si}_3\text{N}_4$  and  $\beta$ - $\text{Si}_3\text{N}_4$  (tab.11.1). The solubility of nitrogen in silicon is very low [76Fro].

### **SOLID PHASES / ISOTHERMAL SECTIONS**

The ternary phase  $\text{Sm}_2\text{Si}_2\text{N}_4$  is described in tab.11.1.

### **REFERENCES**

- [72Kie] R. Kieffer, P. Ettmayer and S. Pajakoff, "On the Mononitrides and on Nitrogen Rich Nitrides of the Rare Earth, 1<sup>st</sup> Comm.", *Monatsh. Chem.* **103** (1972) 1285-1298
- [76Fro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [83Gau] J. Gaude, J. Lang and D. Louer, " $\text{Sm}_2\text{Si}_2\text{N}_4$ , a New Double Nitride of Silicon and Rare Earth", *Rev. Chim. Miner.*, **20** (1983) 523-527
- [85Vil] P. Villars and L. D. Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, OH., 1985)
- [86Mas] T. B. Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer. Soc. Met., Metals Park, OH., 1986)
- [88Gok] A. B. Gokhale and G. J. Abbaschian, "The Si-Sm (Silicon-Samarium) System", *Bull. Alloy Phase Diagr.* **9** (1988) 582-585

Table 11.1: Solid phases in the system Sm - Si - N

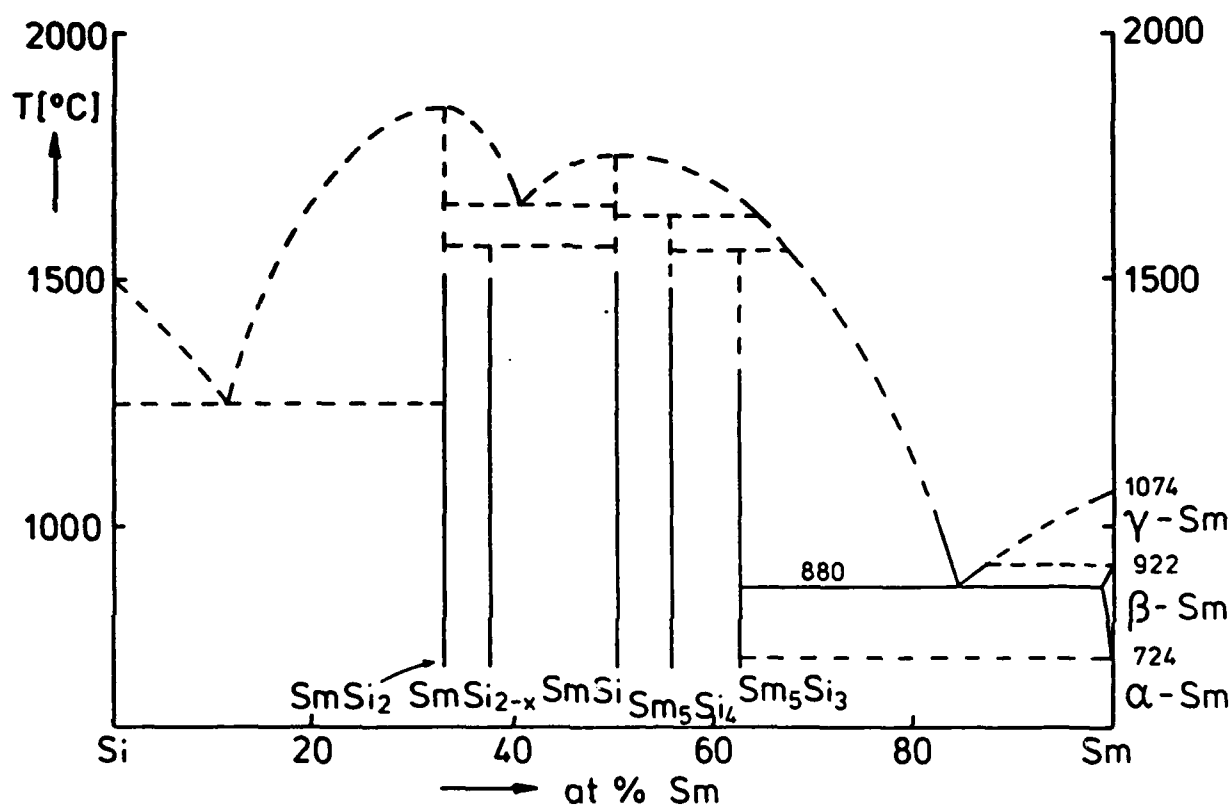
Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\alpha$ -Sm(r) T<734	hR3 $R\bar{3}m$ Sm (C19)	a= 899.6 $\alpha = 23.22^\circ$	[85V11]; powder pattern: ASTM file card # 6-419
$\beta$ -Sm(h) T>734	hP4 P6 <sub>3</sub> /mmc La (A3')	a= 361.99 c= 1168.0	[86Mas]; powder pattern ASTM file card # 37-1446
Sm <sub>3</sub> Si <sub>2</sub>	hP16 P6 <sub>3</sub> /mcm Mn <sub>3</sub> Si <sub>2</sub> (D8 <sub>8</sub> )	a= 856 c= 645	[85V11]
Sm <sub>3</sub> Si <sub>4</sub>	oP36 Pnma Sm <sub>3</sub> Ge <sub>4</sub>	a= 757 b= 1488 c= 778	[85V11]
SmSi	oP8 Pnma FeB (B27)	a= 805.5 b= 388.8 c= 580.4	[85V11]
SmSi <sub>2-x</sub> (Sm <sub>3</sub> Si <sub>5</sub> )	hP3 P6/mmm AlB <sub>2</sub> (C32)	a= 390.3 c= 420.7	[85V11]
SmSi <sub>2</sub> (Sm <sub>2</sub> Si <sub>3</sub> )	tI12 I4 <sub>1</sub> /amd ThSi <sub>2</sub> (C <sub>c</sub> )	a= 408 c= 1351	[85V11]
SmN	cF8 Fm $\bar{3}m$ NaCl (B1)	a= 503.9	[85V11]; powder pattern: ASTM file card # 30-1104
Si	cF8 Fd $\bar{3}m$ C (A4)	a= 542.86	[85V11]; powder pattern: ASTM file card # 5-565

Tab.11.1 continued

$\alpha$ - $\text{Si}_3\text{N}_4$	hP28	a= 781.8	[85V11]; powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
$\beta$ - $\text{Si}_3\text{N}_4$	$\text{Si}_3\text{N}_4$		
	hP14	a= 760.8	[85V11]; powder pattern:
	P6 <sub>2</sub> /m	c= 291.1	ASTM file card # 29-1132
$^*\text{Si}_3\text{Si}_2\text{N}_5$	$\text{Si}_3\text{N}_4$		33-1160
	t**	a= 999.31	[83Gau]; powder pattern:
		c= 483.61	ASTM file card # 38-1291

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Fig.11.1: Phase diagram for the boundary system samarium - silicon



## SYSTEM HOLMIUM - SILICON - NITROGEN (Ho-Si-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria of Ho-Si-N at 1000°C were determined by x-ray analysis [90Wei]. The alloys were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si), silicon (purity: 3N) and holmium (purity 3N) all from Alpha Div., Ventron Corp., USA. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were sealed in evacuated quartz tubes lined with Mo foil and heat treated for 1000h at 1000°C.

### BINARY SYSTEMS

A phase diagram for the system Ho-Si (fig.12.1) is presented in [90Wei]. The intermediate phases are described in tab.12.1. No phase diagrams are reported for Ho-N or Si-N. Under normal pressure HoN is the only stable holmium nitride [72Kie].  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.12.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in the system Ho-Si-N (tab.12.1). The isothermal section at 1000°C (fig.12.2 [90Wei]) shows HoN to coexist with all binary cerium silicides except  $\text{HoSi}_2$ .  $\text{Si}_3\text{N}_4$  coexists with HoN,  $\text{HoSi}_{2-x}$  and  $\text{HoSi}_2$ . Thus silicon nitride in contact with holmium is decomposed at elevated temperatures. The lattice parameters of  $\text{Ho}_2\text{Si}_3$  in equilibrium with HoN increase relative to the value of the binary phase to  $a = 834.07\text{pm}$  and  $c = 645.35\text{pm}$  indicating extended solubility for nitrogen in this phase (fig.12.3). None of the other binary phases shows signs of solubility for the respective third component.

## REFERENCES

- [72Kie] R.Kieffer, P.Ettmayer and S.Pajakoff, "On the Mononitrides and on Nitrogen Rich Nitrides of the Rare Earth, 1<sup>st</sup> Comm.", *Monatsh. Chem.* 103 (1972) 1285-1298
- [76Pro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [90Wei] F.Weitzer, J.C.Schuster, J.Bauer and B.Jouneil, "Phase Equilibria in Ternary Re-Si-N Systems (RE= Sc, Ce, Ho)", *J.Mater.Sci.* 25 (1990)

Table 12.1: Solid phases in the system Ho - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Ho	hP2 P6 <sub>3</sub> /mmc Mg (A3)	a= 357.73 c= 561.58	[85Vil]; powder pattern: ASTM file card # 2-910
Ho <sub>3</sub> Si <sub>2</sub>	hP16 P6 <sub>3</sub> /mcm Mn <sub>3</sub> Si <sub>2</sub> (D8 <sub>8</sub> )	a= 834 c= 622	[85Vil]; powder pattern: ASTM file card # 26-748
Ho <sub>3</sub> Si <sub>4</sub>	oP36 Pnma Sm <sub>3</sub> Ge <sub>4</sub>	a= 733.8 b= 1444.9 c= 762.5	[85Vil]
HoSi(r)	oC8 Cmcm CrB (B33)	a= 422.8 b= 1042.9 c= 380.1	[85Vil]; powder pattern: ASTM file card # 19-561
HoSi(h)	oP8 Pnma FeB (B27)	a= 780.8 b= 380.1 c= 563.3	[85Vil]; powder pattern: ASTM file card # 19-562



Tab.12.1 continued

$\text{HoSi}_{2-x}$ ( $\text{Ho}_x\text{Si}_2$ )	hP3	a= 381.6	[85Vil]; powder pattern:
	P6/mmm	c= 410.7	ASTM file card # 19-560
$\text{HoSi}_2$	$\text{AlB}_2$ (C32)		
	oI12	a= 399	[85Vil]; powder pattern:
	Imma	b= 394	ASTM file card # 13-381
$\text{HoN}$	$\text{GdSi}_2$	c= 1330	
	cF8	a= 487.7	[85Vil]; powder pattern:
	$\text{Fm}\bar{3}\text{m}$		ASTM file card # 15-889
$\text{Si}$	$\text{NaCl}$ (B1)		
	cF8	a= 542.86	[85Vil]; powder pattern:
	$\text{Fd}\bar{3}\text{m}$		ASTM file card # 5-565
$\alpha\text{-Si}_3\text{N}_4$	C (A4)		
	hP28	a= 781.8	[85Vil]; powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
$\beta\text{-Si}_3\text{N}_4$	$\text{Si}_3\text{N}_4$		
	hP14	a= 760.8	[85Vil]; powder pattern:
	$\text{P6}_3/\text{m}$	c= 291.1	ASTM file card # 29-1132
	$\text{Si}_3\text{N}_4$		33-1160

Fig.12.1: Phase diagram for the boundary system holmium - silicon

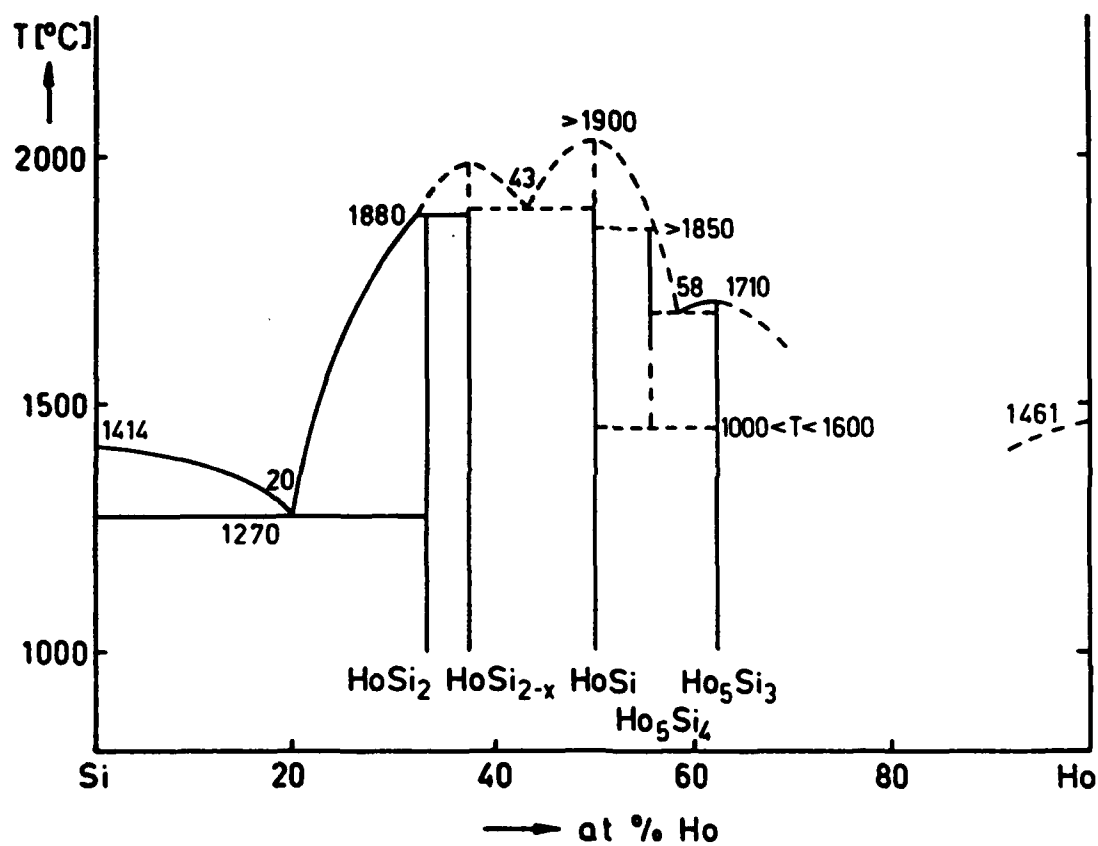


Fig.12.2: Isothermal section observed for the system Ho - Si - N  
at 1000°C (in the absence of external nitrogen pressure)

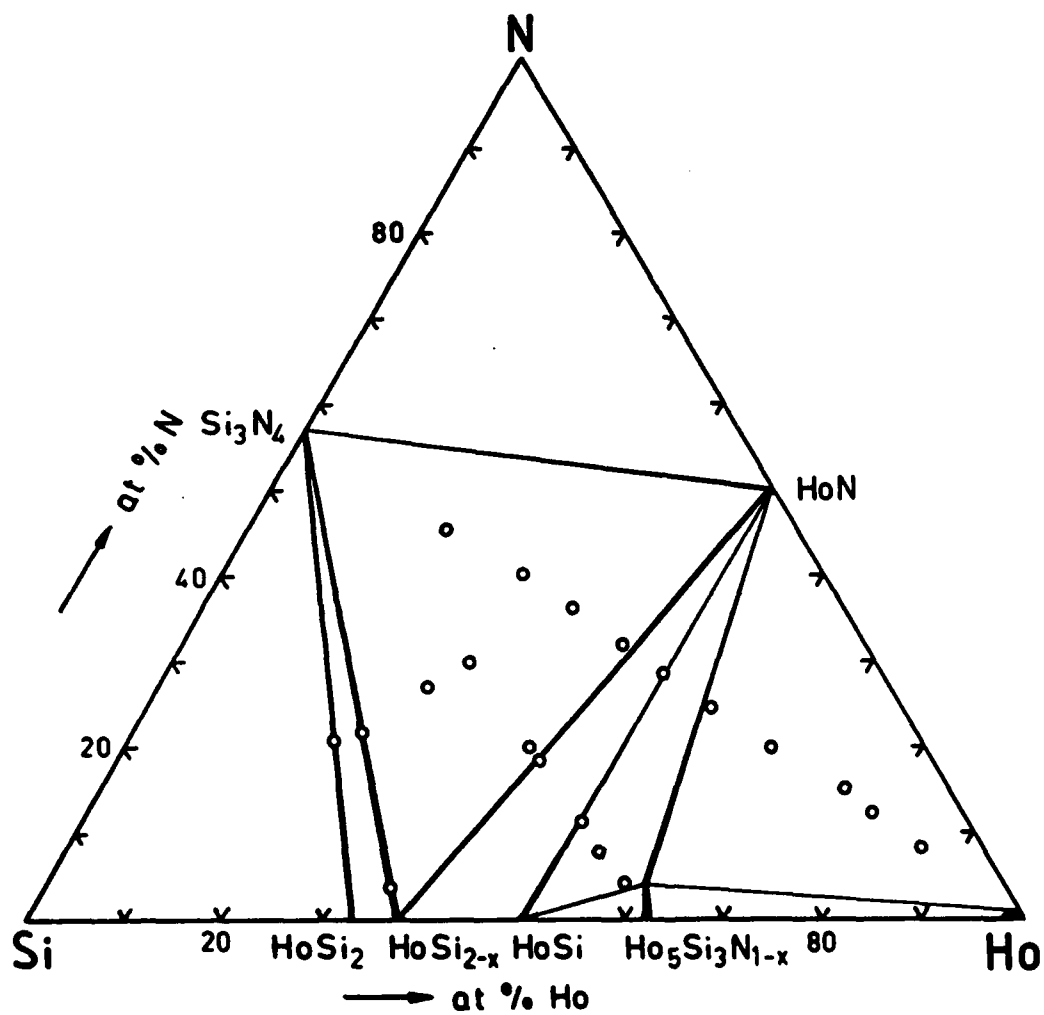
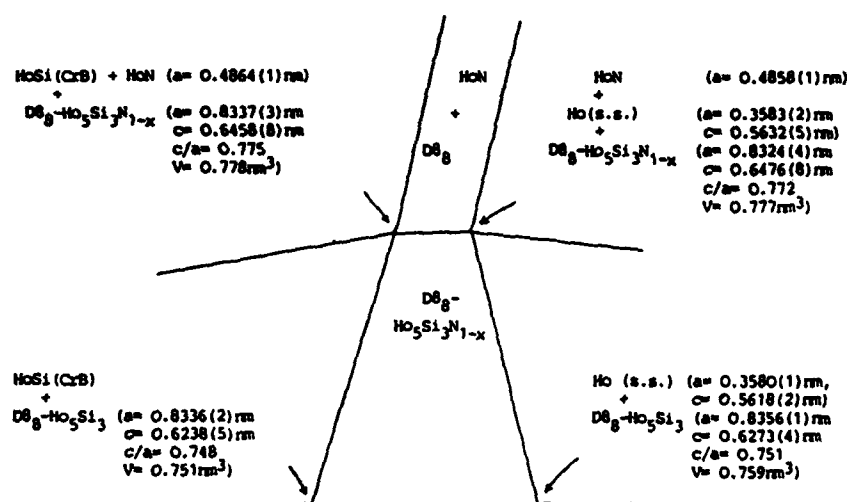


Fig.12.3: The homogeneity region of  $\text{Ho}_5\text{Si}_3\text{N}_{1-x}$  at 1000°C



## SYSTEM TITANIUM - SILICON - NITROGEN (Ti-Si-N)

### INTRODUCTION / EXPERIMENTAL

The isothermal section of Ti-Si-N at 1000°C were calculated from thermodynamic data [84Bey] and are determined by x-ray analysis [85Sch]. The alloys investigated in the latter work were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si), silicon (purity: 3N), titanium (purity: 2N, impurities in ppm: Ca 4000, Al 3500, Fe 1000, C 150, Si 30, other 30) and titanium nitride (purity 2N) all from Alpha Div., Ventron Corp., USA. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 550h at 1000°C or annealed at 1300°C, 48h in a r.f. furnace under argon (purity: 5N+).

### BINARY SYSTEMS

The phase diagram for the binary system Ti-Si given in [86Mas] shows the occurrence of four intermediate phases. However, the phase  $\text{Ti}_2\text{Si}_3$  exists in two modifications (tab.13.1) as found by [69Nic]. The phase  $\text{Ti}_2\text{Si}$  is possibly impurity stabilized [89Paj][89Kiv]. The Ti-Si system was thermodynamically modelled by [89Paj] as well as by [89Vah]. The phase diagram of Ti-N given in [86Mas] needs to be updated (fig.13.1 [90Len]) to account for the newly discovered phases  $\eta\text{-Ti}_3\text{N}_{2-x}$  [86-1Len] and  $\zeta\text{-Ti}_3\text{N}_{2-x}$  [86-2Len]. No phase diagram is reported for Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.13.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Ti-Si-N (tab.13.1). The isothermal section at 1000°C experimentally observed (fig.13.2 [85Sch]) shows  $\text{TiN}_{1-x}$  to be in equilibrium with  $\text{Si}_3\text{N}_4$ ,  $\text{TiSi}$ , and  $\text{Ti}_2\text{Si}_3$  which dissolves considerable amounts of nitrogen as is indicated by the increase of the lattice parameters relative to the values of the

binary compound (fig.13.3).  $TiN_{1-x}$  coexists furthermore with  $\alpha$ -Ti (containing 20 at% nitrogen in solid solution) and thus cuts off any phase fields containing  $\epsilon$ - $Ti_2N$  (fig.13.4). Analogously, the tie line between  $TiSi_2$  and  $Ti_3Si_4$  (containing  $\approx 4$  at% nitrogen in solid solution) confines the occurrence of the phase  $TiSi$  and  $Ti_3Si_4$  to compositions close to the binary Ti-Si. Except for  $Ti_3Si_4$ , lattice parameters of neither titanium silicide coexisting with  $Si_3N_4$  or  $TiN_{1-x}$  are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in these titanium silicides. These results are in perfect agreement with experimental data on the reaction of  $Si_3N_4$  with titanium at  $500^\circ C < T < 2200^\circ C$  [78Bor], [83Ore], [85Kag], [[86Mor], [86Sug], [87Bar], [90Des]; the reaction of titanium silicides with nitrogen [56Bre], [56Kie], [56Now], [69Fit], [89Jos], [90Des]; the reaction of  $TiN_{1-x}$  with silicon [84Kab] and the compatibility of  $TiN_{1-x}$  in contact with  $Si_3N_4$  [81Som], [82Hay], [82Hir], [85Uch] or with  $TiSi_2$  [73Cha], [83Nor], [85Ada], [86Tin]. Using the thermodynamic data in tab.13.2 the phase equilibria at  $1000^\circ C$  can be calculated. At variance with [84Bey], but in agreement with [76Kri] the tie lines resulting for  $1000^\circ C$  confirm the experimentally observed isothermal section (figs.13.2). There is no pressure or temperature range where  $Si_3N_4$  coexists in equilibrium with titanium.

#### MISCELLANEOUS

Silicon nitride is not wet by  $TiSi_2$  at  $1500^\circ C$  [73Cha]. Additions of titanium enhance the nitridation reaction rate of silicon [81Muk].

#### REFERENCES

- [56Bre] L. Brewer and O. Krikorian, "Reactions of Refractory Silicides with Carbon and Nitrogen", J. Electrochem. Soc. 103 (1956) 38-50
- [56Kie] R. Kieffer, F. Benesovsky and B. Lux, Planseeber. Pulvermet. 4 (1956) 30
- [56Now] H. Nowotny, B. Lux and H. Kudielka, "The Behavior of Metal Rich, High Melting Silicides Versus Boron, Carbon, Nitrogen and Oxygen", Monatsh. Chem. 87 (1956) 447-470
- [69Fit] E. Fitzer and K. Reinmuth, "Reaction of High Melting Silicides with Nitrogen and Carbon", Proc 6<sup>th</sup> Int. Plansee Sem. (Reutte, Austria, 1969) p767-802
- [69Nic] J. J. Nickl and H. Sprenger, "New Phases in the Ternary System Titanium-Copper-Silicon", Z. Metallk. 60 (1969) 136-139

- [73Cha] J.A.Champion, B.J.Keene and S.Allen, "Wetting of Refractory Materials by Molten Metallides", *J.Mater.Sci.* 8 (1973) 423-426
- [76Kri] Y.I.Krilov and V.A.Bronnikov, "Thermit Mixtures on the Basis of Exothermal Reactions of BN and  $\text{Si}_3\text{N}_4$  with Metals", *Porosh. Met.* (1) (1976) 52-55
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [78Bor] Y.S.Borisov, A.L.Borisova, Y.A.Kochershinskii and E.A.Shishkin, "Certain Peculiarities of Interaction in the Ti- $\text{Si}_3\text{N}_4$  System under Conditions of Usual and Plasmic Heating", *Poroshk.Met.* (3) (1978) 63-69
- [81Muk] J.Mukerji and S.K.Biswas, "Effect of Iron, Titanium and Hafnium on Second-Stage Nitriding of Silicon", *J.Amer.Ceram.Soc.* 64 (1981) 549-552
- [81Som] S.Somiya, M.Yoshimura and N.Shinohara, "Reactions and Phase Relations in the System Si-Ti-N between 1400°C and 1650°C under 1atm  $\text{N}_2$ ", *Rept.Res.Lab.Eng.Mater.Tokyo Inst.Technol.* (6) (1981) 107-117
- [82Hay] S.Hayashi, T.Hirai, K.Hiraga and M.Hirabayshi, "Microstructure of  $\text{Si}_3\text{N}_4$ -TiN Composites Prepared by Chemical Vapour Deposition", *J.Mater.Sci.* 17 (1982) 3336-3340
- [82Hir] T.Hirai and S.Hayashi, "Preparation and some Properties of Chemically Vapour-Deposited  $\text{Si}_3\text{N}_4$ -TiN Composite", *J.Mater.Sci.* 17 (1982) 1320-1328
- [83Nor] H.Norström, T.Donchev, M.Östling and C.S.Petersson, "TiSi<sub>2</sub>/TiN - A Stable Multilayered Contact Structure for Shallow Implanted Junctions in VSLI Technology", *Physica Scripta* 28 (1983) 633-636
- [83Ore] T.W.Orent and R.A.Wagner, "Investigation of the Chemical Bonding of Cr and Ti to Silicon Nitride", *J.Vac.Sci.Technol.* B1 (1983) 844-849
- [84Bey] R.Beyers, R.Sinclair and M.E.Thomas, "Phase Equilibria in Thin Film Metallisations", *J.Vac.Sci.Technol.* B2 (1984) 781-784
- [84Kab] M.Kabbaj, A.Galerie and M.Caillet, "Wear Resistant and Oxidation Resistant Composite Coatings on Titanium", *Proc.10<sup>th</sup> Int.Symp. Reactivity of Solids* (Dijon, France, 1984) 120-121
- [85Ada] E.D.Adams, K.Y.Ahn and S.B.Brodsky, "Formation of TiSi<sub>2</sub> and TiN during Nitrogen Annealing of Magnetron Sputtered Ti Films", *J.Vac.Sci.Technol.* A3 (1985) 2264-2267
- [85Kag] Y.Kagawa, "Reaction Between Reaction-Bonded  $\text{Si}_3\text{N}_4$  and Titanium Thin Films", *J.Mater.Sci.Lett.* 4 (1985) 1062-1066
- [85Sch] J.C.Schuster and H.Nowotny, "Silicon Nitride and Transition Metals: A Critical Evaluation of Existing Phase Diagram Data Supplemented by New Experimental Results", *Proc.11<sup>th</sup> Int.Plansee Seminar* (Reutte, Austria, 1985) Vol.1, p899-911

- [85Uch] N.Uchida, M.Koizumi and M.Shimada, "Fabrication of  $\text{Si}_3\text{N}_4$  Ceramics with Metal Nitride Additives by Isostatic Hot Pressing", J.Amer. Ceram.Soc. 64 (1981) 549-552
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86-1Len] W.Lengauer, "The Crystal Structure of  $\eta\text{-Ti}_3\text{N}_4$  : An Additional New Phase in the Ti-N System", J.Less Common Met. 125 (1986) 127-134
- [86-2Len] W.Lengauer and P.Ettmayer, "The Crystal Structure of a New Phase in the Titanium-Nitrogen System", J.Less Common Met. 120 (1986) 153-159
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [86Mor] A.E.Morgan, E.K.Broadbent and D.K.Sadana, "Reaction of Titanium with Silicon Nitride under Rapid Thermal Annealing", Appl. Phys.Lett. 49 (1986) 1236-1238
- [86Sug] K.Suganuma, T.Okamoto, Y.Miyamoto, M.Shimada and M.Koizumi, "Joining  $\text{Si}_3\text{N}_4$  to Type 405 Steel with Soft Metal Interlayers", Mater.Sci.Technol. 2 (1986) 1156-1161
- [86Tin] C.Y.Ting, F.M.d'Heurle, S.S.Iyer and P.M.Fryer, "High Temperature Process Limitations on  $\text{TiSi}_2$ ", J.Electrochem.Soc. 133 (1986) 2621-2625
- [87Bar] J.C.Barbour, A.E.T.Kuiper, M.F.C.Willemsen and A.H.Reader, "Thin Film Reaction Between Ti and  $\text{Si}_3\text{N}_4$ ", Appl.Phys.Lett. 50 (1987) 953-955
- [87Len] W.Lengauer and P.Ettmayer, "Some Aspects of the Formation of  $\epsilon\text{-Ti}_3\text{N}_4$ ", Rev.Chim.Miner. 24 (1987) 707-713
- [89Jos] R.V.Joshi et al., "Novel Self Aligned W/TiN/ $\text{TiSi}_2$  Contact Structure for very shallow Junctions and Interconnections", Appl.Phys.Lett. 54 (1989) 1672-1674
- [89Paj] M.Pajunen and J.Kivilahti, "Assessment of the Ti-Si System", paper presented at the CALPHAD Meeting, Stockholm, Sweden, 1989
- [89Kiv] J.Kivilahti, personal communication, 1989
- [89Vah] C.Vahlas, P.Y.Chevalier and E.Blanquet, "A Thermodynamic Evaluation of Four Si-M (M= Mo, Ta, Ti, W) Binary Systems", CALPHAD 13 (1989) 273-292
- [90Des] S.B.Desu and J.A.Taylor, "Reactions which Form Both Silicide and Nitride Layers", J.Amer.Ceram.Soc. 73 (1990) 509-515
- [90Len] W.Lengauer, private communication (to be published)



Table 13.1: Solid phases in the system Ti - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\alpha$ -Ti(r) T<882	hP2 P6 <sub>3</sub> /mmc Mg (A3)	a= 295.08 c= 468.55	[85Vil]; powder pattern: ASTM file card # 5-682
$\beta$ -Ti(h) T>882	cI2 Im $\bar{3}$ m W (A2)	a= 330.65	[85Vil];
Ti <sub>3</sub> Si T<1170	tP32 P4 <sub>2</sub> /n Ti <sub>3</sub> P	a= 1019.6 c= 509.7	[85Vil]; possibly impurity stabilized
Ti <sub>3</sub> Si <sub>2</sub>	hP16 P6 <sub>3</sub> /mcm Mn <sub>3</sub> Si <sub>2</sub> (D8 <sub>8</sub> )	a= 742.9 c= 513.92	[85Vil]; powder pattern: ASTM file card # 29-1362
Ti <sub>5</sub> Si <sub>4</sub> (r)	tP36 P4 <sub>1</sub> 2 <sub>1</sub> 2 Zr <sub>5</sub> Si <sub>4</sub>	a= 670.2 c= 1217.4	[85Vil]; powder pattern: ASTM file card # 27-907
Ti <sub>5</sub> Si <sub>4</sub> (h)	oP* Pbnm	a= 664.5 b= 650.6 c= 1269.0	[69Nic]; powder pattern: ASTM file card # 23-1079
TiSi	oP8 Pnma FeB (B27)	a= 654.4 b= 363.8 c= 499.7	[85Vil]; powder pattern: ASTM file card # 17-424
TiSi <sub>2</sub>	oF24 Fddd TiSi <sub>2</sub> (C54)	a= 826.71 b= 480.00 c= 855.05	[85Vil]; powder pattern: ASTM file card # 2-1120 35-785
$\epsilon$ -Ti <sub>2</sub> N(r) T<1080	tP6 P4 <sub>2</sub> /mmn TiO <sub>2</sub>	a= 494.28 c= 303.57	[85Vil]; powder pattern: ASTM file card # 17-386 31-33 at% N [87Len]
$\eta$ -Ti <sub>3</sub> N <sub>2-x</sub> (h) 1066<T<1103	hR6 R $\bar{3}$ m AgCrSe <sub>2</sub>	a= 297.95 c= 2896.5	[86-1Len]; gives powder pattern 29 at% N [86-1Len]

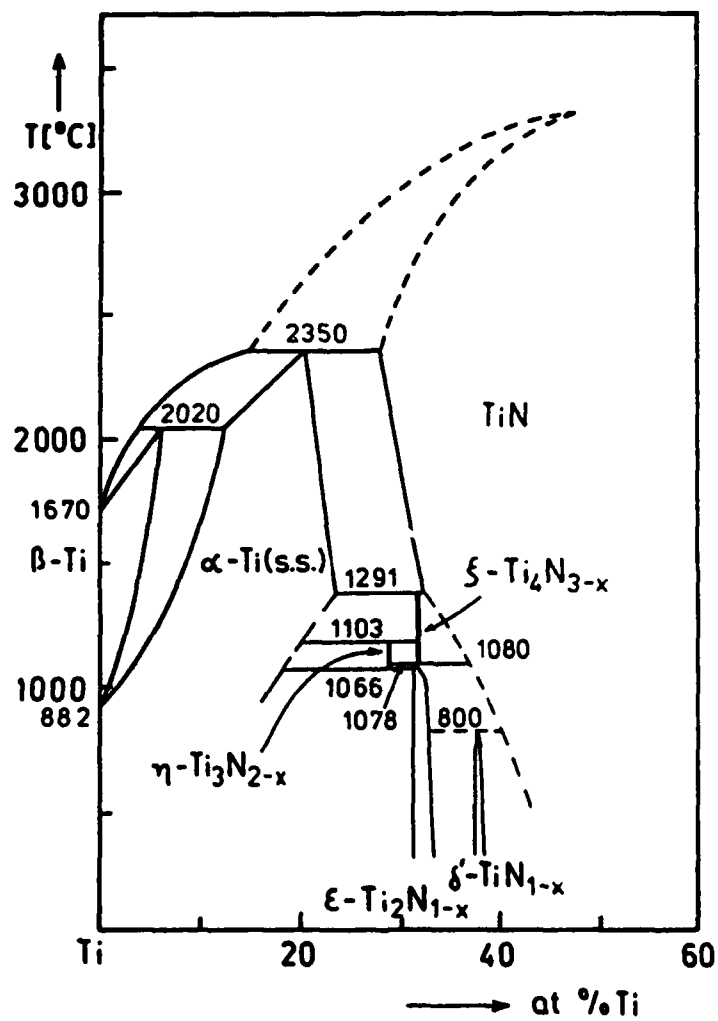
Tab.13.1 continued

$\zeta$ -Ti <sub>3</sub> N <sub>2-x</sub> (h)	hR8	a= 298.09	[86-2Len];
1078<T<1291	R $\bar{3}$ m	c= 2166.42	gives powder pattern
	Ti <sub>3</sub> S <sub>12</sub>		31.5 at% N [86-2Len]
$\delta$ -TiN <sub>1-x</sub> (r)	tI16	a= 414.0	[85Vil]; powder pattern:
T<800	I4 <sub>1</sub> /amd	c= 880.5	ASTM file card # 23-1455
(metastable)			38 at% N [87Len]
TiN <sub>1-x</sub>	CF8	a= 423.9	[85Vil]; powder pattern:
	Fm $\bar{3}$ m		ASTM file card # 38-1420
	NaCl (B1)		
Si	CF8	a= 542.86	[85Vil]; powder pattern:
	Fd $\bar{3}$ m		ASTM file card # 5-565
	C (A4)		
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28	a= 781.8	[85Vil]; powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si <sub>3</sub> N <sub>4</sub>		
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14	a= 760.8	[85Vil]; powder pattern:
	P6 <sub>3</sub> /m	c= 291.1	ASTM file card # 29-1132
	Si <sub>3</sub> N <sub>4</sub>		33-1160

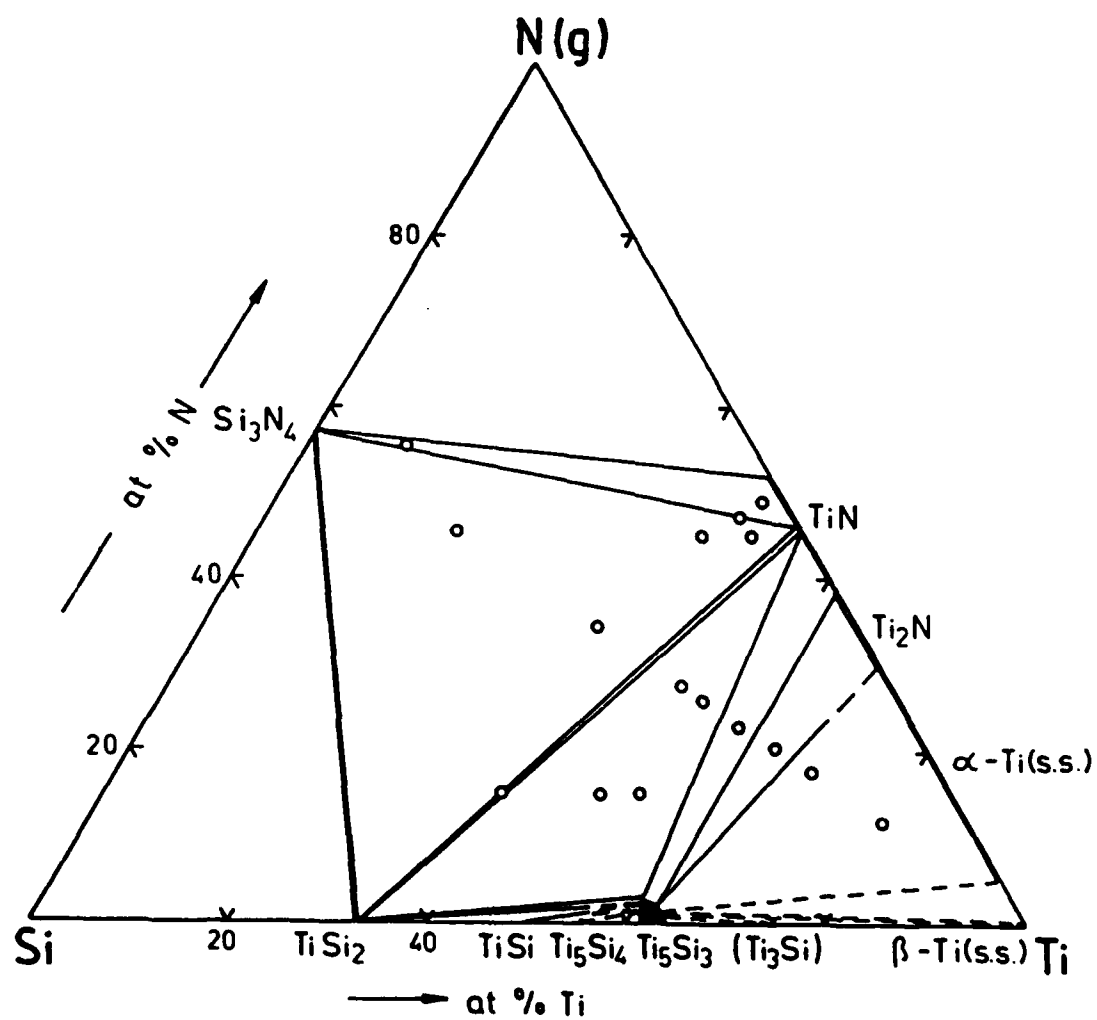
Tab.13.2: Thermodynamic data for the solid phases in Ti - Si - N

phase	$\Delta G_f^\circ$ (J/gramatom)	Comment
.1429 Si <sub>3</sub> N <sub>4</sub>	-124602 + 57.95 T	[76Fro]
.3333 TiSi <sub>2</sub>	-56967 + 2.23725 T	[89Vah]
.5000 TiSi	-68000 - 0.04119 T	[89Vah]
.5000 Ti <sub>3</sub> Si <sub>4</sub>	-71000 - 0.79164 T	[89Vah]
.1250 Ti <sub>3</sub> Si <sub>4</sub>	-72409.5 - 0.31694 T	[89Vah]
.2500 Ti <sub>3</sub> Si	-66565.2 + 11.5143 T	[89Vah]
.5000 TiN	-167883 + 46.4424 T	(25°C<T<882°C) [76Fro]
	-169138.2 + 47.4884 T	(882°C<T<1200°C) [76Fro]

Fig.13.1: Phase diagram of the boundary system titanium - nitrogen



**Fig.13.2: Isothermal section observed in the system Ti - Si - N  
at 1000°C (in the absence of external nitrogen pressure)**



**Fig.13.3: Lattice parameters,  $c/a$  ratios and unit cell volumes of the  $D8_8$ -type  $Ti_5Si_3N_{1-x}$  phase field homogeneity limits at 1000°C**

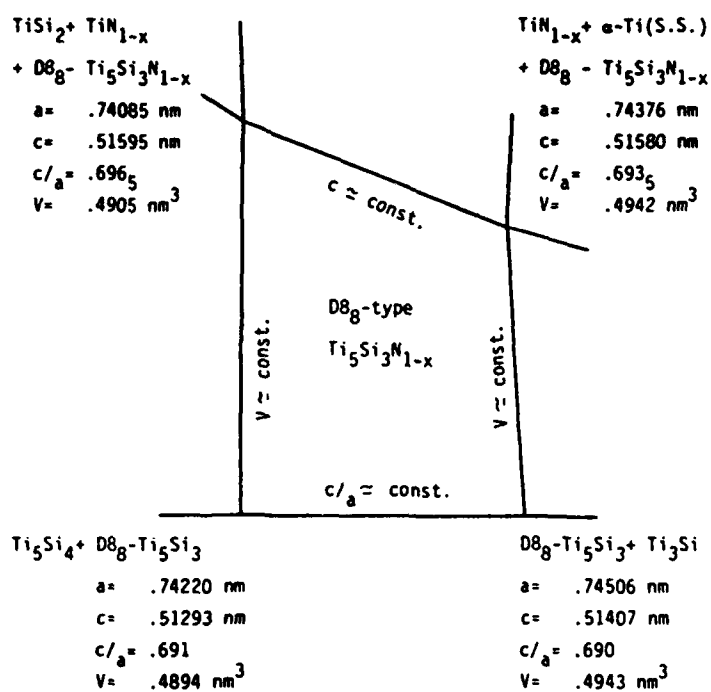
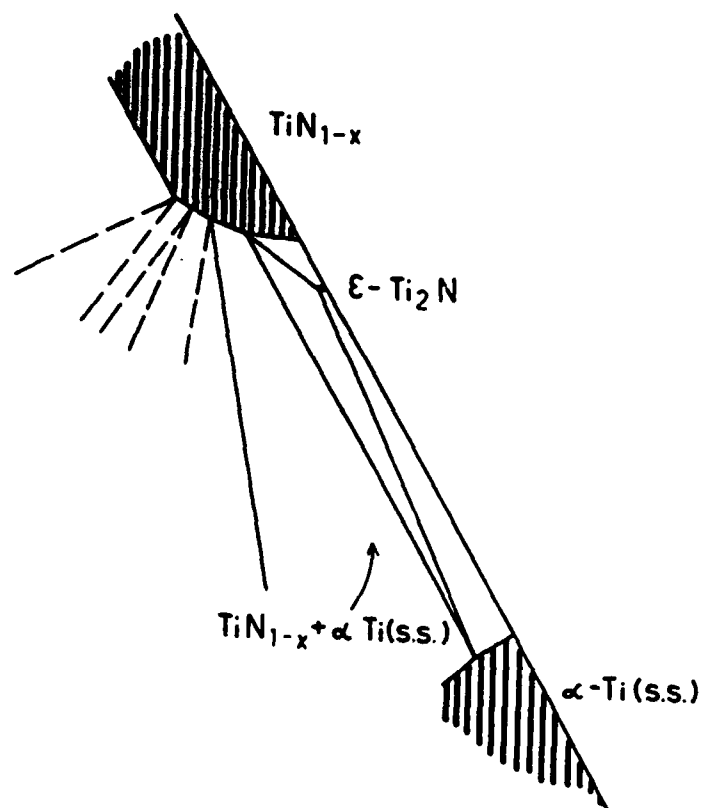


Fig.13.4: Detail of the phase field partition at 1000°C in Ti-Si-N close to the binary Ti-N (schematic)



## SYSTEM ZIRCONIUM - SILICON - NITROGEN (Zr-Si-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria of Zr-Si-N at 1000°C and 1300°C were determined by x-ray analysis [85-1Sch]. The alloys were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si), silicon (purity: 3N), zirconium (purity: 3N) all from Alpha Div., Ventron Corp., USA and zirconium nitride (purity 2N; from Materials Research Corp., USA. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 400h at 1000°C or annealed at 1300°C, 48h in a r.f. furnace under argon (purity: 5N+).

### BINARY SYSTEMS

The phase diagram for the binary system Zr-Si given in [86Mas] is a reproduction of [76Kub] which is based on [53Lun]. In the more recent experimental investigation by [76Koc], which is reproduced in [76Mof], the phase  $\text{Zr}_2\text{Si}_3$  is found to decompose below 1745°C into  $\text{Zr}_2\text{Si}_2$  and  $\text{Zr}_2\text{Si}$ . Furthermore, the composition of the intermediate phase most rich in zirconium is corrected from  $\text{Zr}_2\text{Si}$  to  $\text{Zr}_3\text{Si}$ . Using high purity materials (Zr bar, purity: 3N, impurities in ppm: O 450, H 260, C < 200, Hf < 200, Cr 60, Al 52, Si 45, other < 30, from Cezus Puk Ugine, France; Si ingot, purity: 6N, from Alpha Div., Ventron Corp., USA) the decomposition of  $\text{Zr}_2\text{Si}_3$  formed upon melting was corroborated [85-2Sch] but the occurrence of a zirconium silicide more rich in Zr than  $\text{Zr}_2\text{Si}$  could not be confirmed. Thus it is likely, that the phase  $\text{Zr}_2\text{Si}$  is impurity stabilized like the analogous phase in the Ti-Si system [89Paj], [89Kiv]. It was noted furthermore [85-2Sch], that  $\text{ZrSi}(h)$  having CrB type structure transforms only in Si rich ZrSi alloys into  $\text{ZrSi}(r)$  having FeB type structure, but not in Zr rich ZrSi alloys where it exists at 1000°C even after annealing for 550h. The phase diagram of Zr-N is given in [86Mas]. No phase diagram is reported for Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab. 14.1). The solubility of nitrogen in silicon is very low [76Fro].

## SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Zr-Si-N (tab.14.1), but  $Zr_3Si_2(h)$  is stabilized by nitrogen to lower temperatures. Two experimentally determined isothermal sections are reported [85Sch]: At 1000°C as well as 1300°C (figs.14.1 and 14.2 resp.).  $Zr_3Al_2N_{1-x}$  coexists at both temperatures with  $ZrN_{1-x}$ ,  $Zr_2Si$ ,  $Zr_3Si_2$ ,  $Zr_5Si_3$  and  $ZrSi$  (CrB). Relative to the binary compound (tab.14.1) the lattice parameters are increased to  $a = 789.22$  pm,  $c = 564.77$  pm (coex. with  $ZrN_{1-x}$ ). At 1000°C  $Si_3N_4$  coexist with  $ZrN_{1-x}$ ,  $ZrSi_2$  and  $ZrSi$  (FeB); at 1300°C no tie line exists between  $Si_3N_4$  and  $ZrSi$ . These data confirm earlier reports on the interaction of  $Si_3N_4 + Zr$  [56-1Bre][76Kri],  $Si + ZrN_{1-x}$  [66Yas],  $Zr_{0.625}Si_{0.375} + ZrN_{1-x}$  (fig.14.3 [56Now]) as well as on the coexistence of  $Si_3N_4 + ZrN_{1-x}$  [85Uch]. With the exception of the above mentioned phase  $Zr_3Si_2N_{1-x}$ , in ternary alloys lattice parameters of neither binary zirconium silicide,  $Si_3N_4$  or  $ZrN_{1-x}$  are altered with respect to the values of the pure binary alloys indicating virtual insolubility of the resp. third component.

The thermodynamic data for zirconium silicides in tab.14.2 are taken from [56-2Bre] (cited in part by [82Mur]) who critically reviewed and supplemented the measurements by [55Rob] rather than just citing their data (as done in more recent compilations, e.g. [60Pop], [70Kar], [76Alc]). However, since the temperature dependency of the data for zirconium silicides are not known, only rough estimates are possible for the tie lines occurring in the ternary Zr-Si-N. The results of these estimates are generally consistent with the experimentally observed isothermal sections (figs.14.1 and 14.2). There is no pressure or temperature range where  $Si_3N_4$  coexists in equilibrium with zirconium.



## REFERENCES

- [53Lun] C.E.Lundin, D.J.McPershon and M.Hansen, "The System Zirconium-Silicon", Trans.Met.Soc.AIME 45 (1953) 901-914
- [55Rob] D.A.Robins and I.Jenkins, "The Heats of Formation of Some Transition Metal Silicides", Acta Met.3 (1955) 598-604
- [56-1Bre] L.Brewer and O.Krikorian, "Reactions of Refractory Silicides with Carbon and Nitrogen", J.Electrochem.Soc.103 (1956) 38-50
- [56-2Bre] L.Brewer and O.Krikorian, "Heats of Formation of Refractory Silicides", Report to the U.S.At.Energy Comm. under contract W-7405-Eng-48 (1956)
- [56Now] H.Nowotny, B.Lux and H.Kudielka, "The Behavior of Metal Rich, High Melting Silicides Versus Boron, Carbon, Nitrogen and Oxygen", Monatsh.Chem.87 (1956) 447-470
- [60Pop] P.Popper "Special Ceramics" (Heywood & Co, London, 1960) p203
- [61Sch] O.Schob, H.Nowotny and F.Benesovsky, "Structure Determination of Phases in the Systems Zr-Al-Si and Hf-Al-Si {ZrAl (Si), HfSi(Al), Hf(Si,Al), Zr<sub>3</sub>Si<sub>2</sub>, Hf<sub>3</sub>Si<sub>2</sub>}", Monatsh.Chem.92 (1961) 1218-1226
- [66Pfe] H.U.Pfeifer and K.Schubert, "Crystal Structure of Zr<sub>3</sub>Si<sub>2</sub>", Z.Metallk.57 (1966) 884-888
- [66Yas] G.A.Yasinskaya, "The Wetting of Refractory Carbides, Borides and Nitrides by Molten Metals", Poroshk.Met.(7)(1966) 53-56
- [70Kar] M.K.Karapet'yants and M.K.Karapet'yants, "Handbook of Thermodynamic Constants of Inorganic and Organic Compounds" (Ann Arbor-Humphrey Sci.Publ., Ann Arbor, MI, 1970)
- [76Alc] C.B.Alcok, K.T.Jacob and S.Zador, "Thermochemical Properties" in "Zirconium: Physico Chemical Properties of its Compounds and Alloys", At.Ener.Rev., Spec.Issue #6 (IAEA, Vienna, Austria, 1976) 7-65
- [76Koc] Y.A.Kocherzinskii, O.G.Kulik and E.A.Shishkin, "Phase Diagram of Zirconium-Silicon System", Metallofizika,64 (1976) 48-52
- [76Kri] Y.I.Krilov and V.A.Bronnikov, "Thermit Mixtures on the Basis of Exothermal Reactions of BN and Si<sub>3</sub>N<sub>4</sub> with Metals", Poroshk.Met.(1) (1976) 52-55
- [76Kub] O.Kubaschewski-von Goldbeck, "Phase Diagrams" in "Zirconium: Physico Chemical Properties of its Compounds and Alloys", At.Ener.Rev., Spec.Issue #6 (IAEA, Vienna, Austria, 1976) p118-120
- [76Mof] W.Moffatt, "The Handbook of Binary Phase Diagrams", (General Electric Comp., Schenectady, NY, 1976 and updates)
- [76Pro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [82Mur] S.P.Murarka, "Heats of Formation of Transition Metal Silicides" Mater.Lett.1 (1982) 26-28
- [85-1sch] J.C.Schuster and H.Nowotny, "Silicon Nitride and Transition Metals: A Critical Evaluation of Existing Phase Diagram Data Supplemented by New Experimental Results", Proc.11<sup>th</sup> Int.Plansee Seminar (Reutte, Austria, 1985) Vol.1, p899-911

- [85-2Sch] J.C.Schuster in "Boron Nitride and Silicon Nitride Systems",  
I Annual Report to the European Research Office of the USA  
under contract DAJA84-C-0038 (1985)
- [85Uch] N.Uchida, M.Koizumi and M.Shimada, "Fabrication of Si<sub>3</sub>N<sub>4</sub> Ceramics  
with Metal Nitride Additives by Isostatic Hot Pressing", J.Amer.  
Ceram.Soc. 64 (1981) 549-552
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic  
Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH.,  
1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc.  
Met., Metals Park, OH., 1986)
- [89Paj] M.Pajunen and J.Kivilahti, "Assessment of the Ti-Si System",  
paper presented at the CALPHAD Meeting, Stockholm, Sweden, 1989
- [89Kiv] J.Kivilahti, personal communication, 1989

Table 14.1: Solid phases in the system Zr - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\alpha$ -Zr(r) T<863	hP2 P6 <sub>3</sub> /mmc Mg (A3)	a= 323.2 c= 514.7	[85Vil]; powder pattern: ASTM file card # 5-665
$\beta$ -Zr T>863	cI2 Im $\bar{3}$ m W (A2)	a= 356.8	[85Vil]; powder pattern: ASTM file card # 34-657
Zr <sub>3</sub> Si	tP32 P4 <sub>2</sub> /n Ti <sub>3</sub> P	a= 1101 c= 545	[85Vil]; possibly impurity stabilized
Zr <sub>2</sub> Si	tI12 I4/mcm Al <sub>2</sub> Cu (C16)	a= 660.9 c= 529.8	[85Vil]; powder pattern: ASTM file card # 25-757
Zr <sub>3</sub> Si <sub>2</sub> (h) T>1745	hP16 P6 <sub>3</sub> /mcm Mn <sub>3</sub> Si <sub>2</sub> (D8 <sub>6</sub> )	a= 788.6 c= 555.8	[85Vil]; powder pattern: ASTM file card # 6-582
Zr <sub>3</sub> Si <sub>2</sub>	tP10 P4/mbm U <sub>3</sub> Si <sub>2</sub> (D5 <sub>6</sub> )	a= 708.2 c= 371.5	[85Vil]; powder pattern: ASTM file card # 14-368
Zr <sub>3</sub> Si <sub>4</sub>	tP36 P4 <sub>1</sub> 2 <sub>1</sub> 2 Zr <sub>3</sub> Si <sub>4</sub>	a= 712.25 c= 1300.0	[85Vil]; powder pattern: given in [66Pfe]
ZrSi(r) T<1460	oP8 Pnma FeB (B27)	a= 699.5 b= 378.6 c= 529.6	[85Vil]; powder pattern: ASTM file card # 9-226
ZrSi(h) T>1460	oC8 Cmcm CrB (B33)	a= 375.4 b= 989.2 c= 374.6	[61Sch]; gives powder pattern
ZrSi <sub>2</sub>	oC12 Cmcm ZrSi <sub>2</sub> (C49)	a= 372.1 b= 1468 c= 368.3	[85Vil]; powder pattern: ASTM file card # 32-1499

Tab.14.1 continued

$ZrN_{1-x}$	cF8	a= 458.5	[85Vil]; powder pattern:
	Fm $\bar{3}m$		ASTM file card # 2-956,
	NaCl (B1)		31-1493, 35-753
Si	cF8	a= 542.86	[85Vil]; powder pattern:
	Fd $\bar{3}m$		ASTM file card # 5-565
	C (A4)		
$\alpha-Si_3N_4$	hP28	a= 781.8	[85Vil]; powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	$Si_3N_4$		
$\beta-Si_3N_4$	hP14	a= 760.8	[85Vil]; powder pattern:
	P6 $_3/m$	c= 291.1	ASTM file card # 29-1132
	$Si_3N_4$		33-1160

Tab.14.2: Thermodynamic data for the solid phases in Zr - Si - N

phase	$\Delta G_f^\circ$ (J/gramatom)	Comment
.1429 $Si_3N_4$	-124602 + 57.95 T	[76Fro]
.3333 $ZrSi_2$	$\Delta H_f^{298} = -53000$	[56-2Bre]
.5000 $ZrSi$	$\Delta H_f^{298} = -77400$	[56-2Bre]
.1111 $Zr_3Si_4$	$\Delta H_f^{298} = -78000$	[56-2Bre]
( $Zr_3Si_4$ )		
.2000 $Zr_2Si_3$	$\Delta H_f^{298} = -77000$	[56-2Bre]
.1250 $Zr_5Si_8$	$\Delta H_f^{298} = -72175$	[56-2Bre]
.3333 $Zr_2Si$	$\Delta H_f^{298} = -69730$	[56-2Bre]
.5000 $ZrN$	-183230 + 48.325 T	[76Fro]

**Fig.14.1: Isothermal section observed in the system Zr - Si - N  
at 1000°C (in the absence of external nitrogen pressure)**

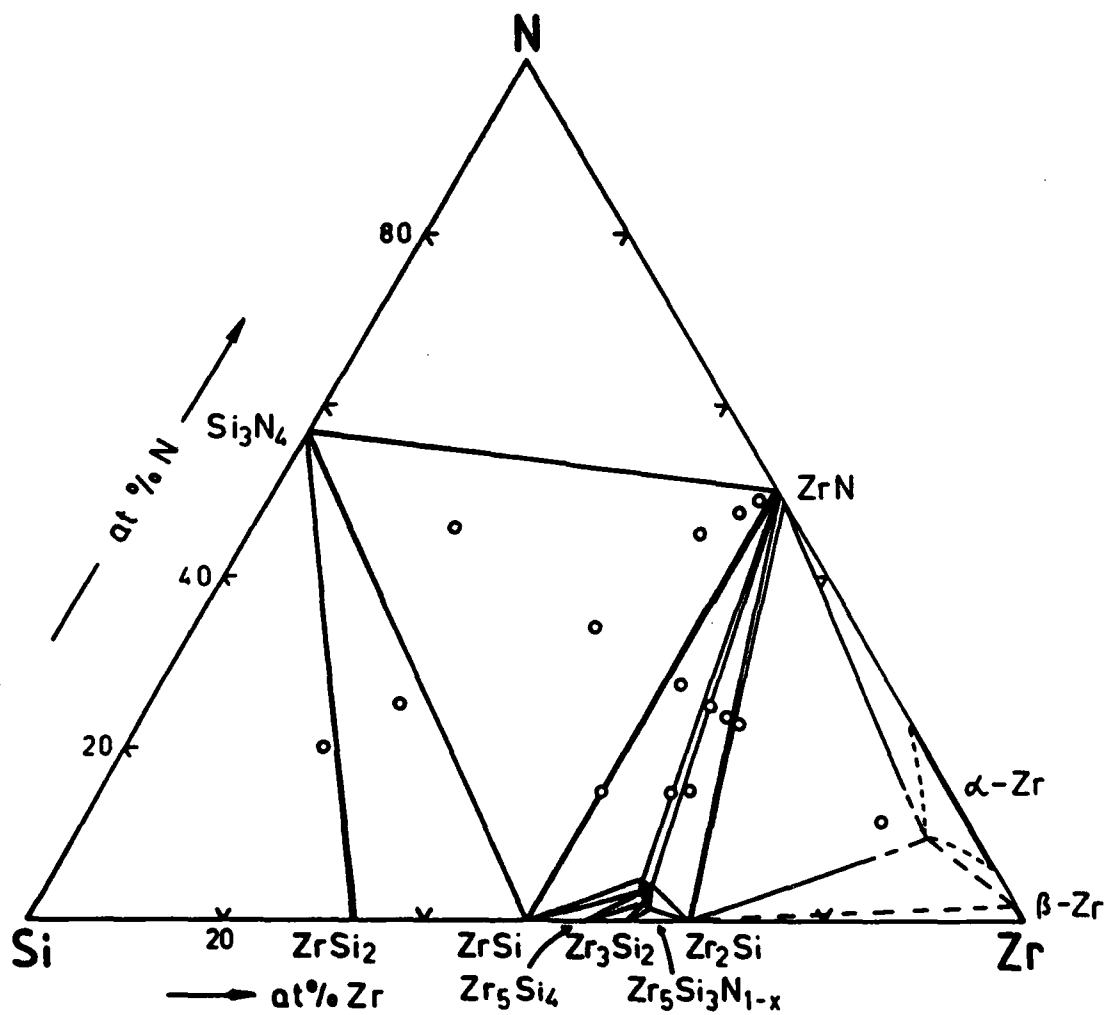


Fig.14.2: Isothermal section observed in the system Zr - Si - N  
at 1300°C (under argon)

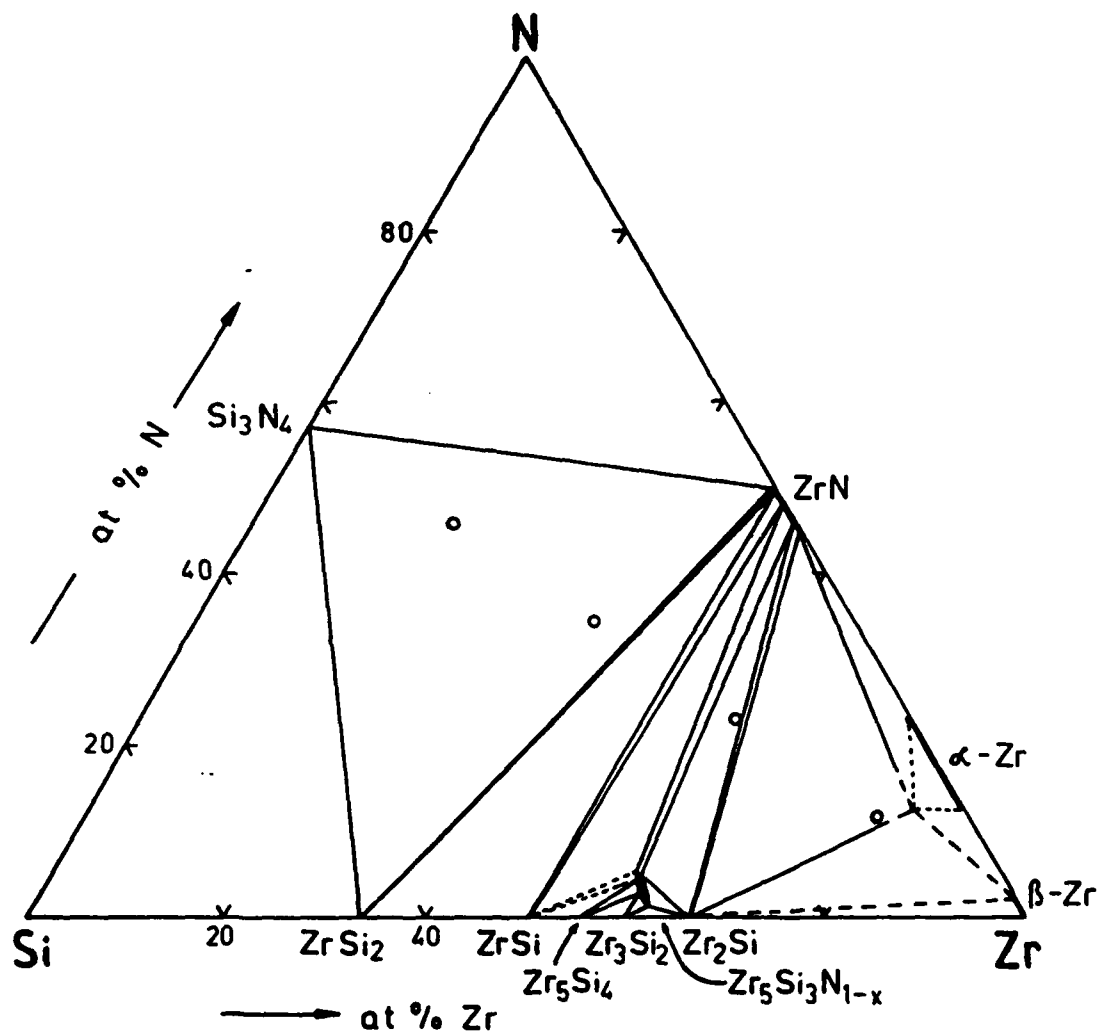
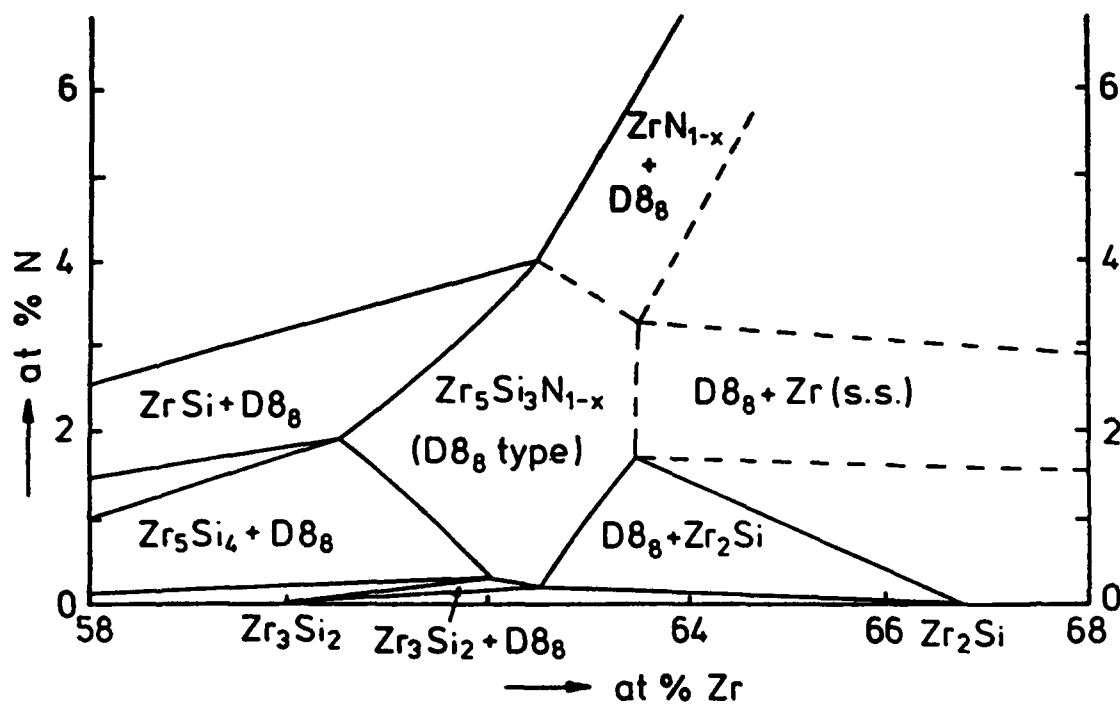


Fig.14.3 The phase field of  $\text{Zr}_5\text{Si}_3\text{N}_{1-x}$  at 1400°C



## SYSTEM HAFNIUM - SILICON - NITROGEN (Hf-Si-N)

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### INTRODUCTION / EXPERIMENTAL

Phase equilibria of Hf-Si-N between 1000°C and 1300°C were determined by x-ray analysis [87Sch],[88Sch]. The alloys investigated in were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si), silicon (purity: 3N) and hafnium (purity: 3N) all from Alpha Div., Ventron Corp., USA as well as hafnium nitride (purity: 2N; from Materials Research Corp., USA). Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 400h at 1000°C or annealed at 1500°C, 48h in a r.f. furnace under argon (purity: 5N+).

### BINARY SYSTEMS

For the system Hf-Si the phase diagram of [69Rud] (reproduced by [76Mof] as well as [89Gok]) is preferred over the diagram compiled by [81Kub] (reproduced in [86Mas]). According to [69Rud] neither  $\text{Hf}_5\text{Si}_3$  ( $\text{Mn}_5\text{Si}_3$ -type) nor  $\text{Hf}_2\text{Si}$  ( $\text{Ti}_2\text{P}$  type) are binary equilibrium phases (tab.15.1). The phase diagram of Hf-N (fig.15.1 [90Oka]) is based on [69Rud] but modified to account for the results of [70Rud] and [73Bil]. No phase diagram is reported for Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.15.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Hf-Si-N (tab.15.1). Isothermal sections are reported for 1000°C and for 1300°C (fig.15.2 [87Sch][88Sch]). At both temperatures  $\text{HfN}_{1-x}$  is the dominating phase coexisting with  $\text{Si}_3\text{N}_4$  as well as all binary silicides. These data confirm earlier reports on the reaction of  $\text{Si}_3\text{N}_4$  with hafnium [81Muk] and on the coexistence of  $\text{Si}_3\text{N}_4$  with HfN during hot pressing at 1850°C [85Uch]. In ternary alloys lattice parameters of neither binary hafnium



silicide,  $\text{Si}_3\text{N}_4$  or  $\text{HfN}_{1-x}$  are altered with respect to the values of the pure binary alloys indicating virtual insolubility of the resp. third component.

Only limited thermodynamic data are available for binary hafnium silicides (tab.15.2). These allow only rough estimates of the tie lines which, however, compare favorably with the experimentally observed equilibria. There is no pressure or temperature range where  $\text{Si}_3\text{N}_4$  coexists in equilibrium with hafnium.

## REFERENCES

- [69Rud] E. Rudy, "Compendium of Phase Diagram Data", Report AFML-TR-65-2 Part V (Wright Patterson AFB, OH., USA, 1969)
- [70Rud] E. Rudy, "The Crystal Structures of  $\text{Hf}_3\text{N}_4$  and  $\text{Hf}_2\text{N}_3$ ", Met. Trans. 1 (1970) 1249-1252
- [73Bil] M. Billy and B. Teyssedre, "Contribution to the Investigation of the System Hafnium-Nitrogen", Bull. Soc. Chim. Fr., 5 (1973) 1537-1540
- [76Mof] W. Moffatt, "The Handbook of Binary Phase Diagrams", (General Electric Comp., Schenectady, NY, 1976 and updates)
- [76Fro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [81Kub] O. Kubaschewski-von Goldbeck, "Phase Diagrams" in "Hafnium: Physico Chemical Properties of its Compounds and Alloys", At. Ener. Rev., Spec. Issue #8 (IAEA, Vienna, Austria, 1981) p 97-99
- [81Muk] J. Mukerji and S. K. Biswas, "Effect of Iron, Titanium and Hafnium on Second Stage Nitriding of Silicon", J. Amer. Ceram. Soc. 64 (1981) 549-552
- [82Mur] S. P. Murarka, "Heats of Formation of Transition Metal Silicides", Mater. Lett. 1 (1982) 26-28
- [85Uch] N. Uchida, M. Koizumi and M. Shimada, "Fabrication of  $\text{Si}_3\text{N}_4$  Ceramics with Metal Nitride Additives by Isostatic Hot Pressing", J. Amer. Ceram. Soc. 64 (1981) 549-552
- [85Vil] P. Villars and L. D. Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, OH., 1985)
- [86Mas] T. B. Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer. Soc. Met., Metals Park, OH., 1986)
- [87Sch] J. C. Schuster in "Boron Nitride and Silicon Nitride Systems", 3<sup>d</sup> Annual Report to the European Research Office of the USA under Contract DAJA84-C-0038 (1987)
- [88Sch] J. C. Schuster, F. Weitzer, J. Bauer and H. Nowotny, "Joining of Silicon Nitride Ceramics to Metals: The Phase Diagram Base", Mater. Sci. Engin. A105/106 (1988) 201-206
- [89Gok] A. B. Gokhale and G. A. Abbaschian, "The Hf-Si (Hafnium-Silicon) System", Bull. Alloy Phase Diagrams 10 (1989) 390-393
- [90Oka] H. Okamoto, "The Hf-N (Hafnium-Nitrogen) System", Bull. Alloy Phase Diagrams 11 (1990) 146-149

Table 15.1: Solid phases in the system Hf - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\alpha$ -Hf(r) T<1743	hP2 P6 <sub>3</sub> /mmc Mg (A3)	a= 319.8 c= 506.1	[85V11];powder pattern: ASTM file card # 38-1478
$\beta$ -Hf(h) T>1743	cI2 Im $\bar{3}$ m W (A2)	a= 361.5	[85V11];
Hf <sub>2</sub> Si	tI12 I4/mcm Al <sub>2</sub> Cu (C16)	a= 655.3 c= 518.6	[85V11];powder pattern: ASTM file card # 12-467 25-371
Hf <sub>3</sub> Si <sub>2</sub>	tP10 P4/mbm (D5 <sub>5</sub> ) U <sub>3</sub> Si <sub>2</sub>	a= 698.8 b= 367.5	[85V11];powder pattern: ASTM file card # 14-427
Hf <sub>5</sub> Si <sub>4</sub>	tP36 P4 <sub>1</sub> 2 <sub>1</sub> 2 Zr <sub>5</sub> Si <sub>4</sub>	a= 703.9 c= 1283	[85V11];
HfSi	oP8 Pnma FeB (B27)	a= 688.9 b= 377.2 c= 522.3	[85V11];powder pattern: ASTM file card # 13-369
HfSi <sub>2</sub>	oC12 Cmcm ZrSi <sub>2</sub> (C49)	a= 367.2 b= 1457 c= 364.1	[85V11];powder pattern: ASTM file card # 10-202 38-1373
Hf <sub>3</sub> N <sub>2</sub> (h) 750<T<2000	hR6 R $\bar{3}$ m AgCrSe <sub>2</sub>	a= 320.6 c= 2326	[85V11];powder pattern: ASTM file card # 23-1097
Hf <sub>3</sub> N <sub>2</sub> (h) 750+ <T<2250	hR8 R $\bar{3}$ m Ti <sub>3</sub> S <sub>12</sub>	a= 321.4 c= 3112	[85V11];powder pattern: ASTM file card # 24-465
HfN <sub>1-x</sub>	cF8 Fm $\bar{3}$ m NaCl (B1)	a= 451.18	[85V11];powder pattern: ASTM file card # 33-592

Tab.15.1 continued

Si	cF8 Fd $\bar{3}m$ C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si $_3$ N $_4$	hP28 P31c Si $_3$ N $_4$	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ -Si $_3$ N $_4$	hP14 P6 $_3/m$ Si $_3$ N $_4$	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160

Tab.15.2: Thermodynamic data for the solid phases in Hf - Si - N

phase	$\Delta G_f^\circ$ (J/gramatom)	Comment
.1429 Si $_3$ N $_4$	-124602 + 57.95 T	[76Fro]
.3333 HfSi $_2$	$\Delta H_f^{298} = -50208$	[82Mur]
.5000 HfSi	$\Delta H_f^{298} = -71130$	[82Mur]
.1250 Hf $_3$ Si $_2$ (Hf $_3$ Si $_4$ + Hf $_3$ Si $_2$ )	$\Delta H_f^{298} = -69820$	[82Mur]
.2500 Hf $_3$ Si	$\Delta H_f^{298} = -62760$	[82Mur]
.5000 HfN	-1845105 + 42.48 T	[76Fro]

Fig.15.1: Phase diagram of the boundary system hafnium - nitrogen

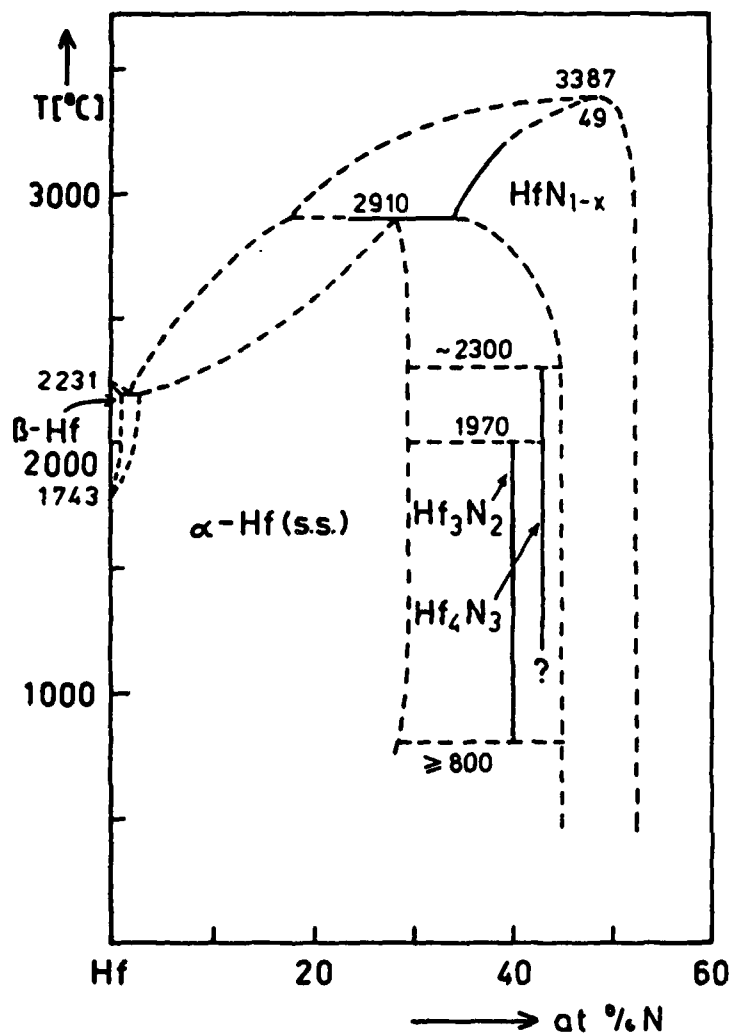
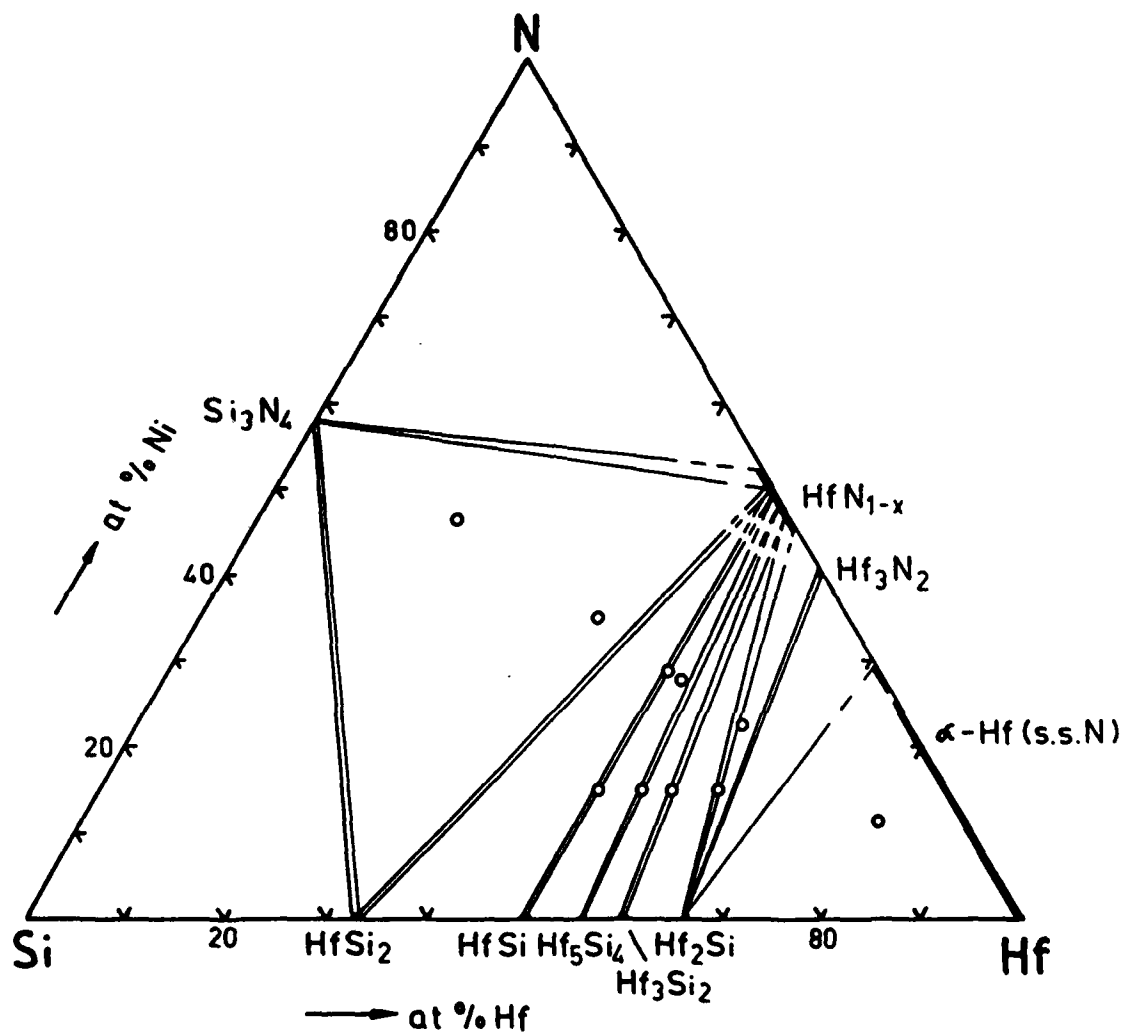


Fig.15.2: Isothermal section observed in the system Hf - Si - N  
at 1300°C under argon (at 1000°C identical tie lines exist)



## SYSTEM VANADIUM - SILICON - NITROGEN (V-Si-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria of V-Si-N at 1000°C and 1500°C were determined by x-ray analysis [85Sch],[86And]. The alloys investigated in the former work were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si), silicon (purity: 3N) and vanadium (purity: 2N5; impurities in ppm: C 900, Si 800, Cr 600, Fe 500, Al 200, others < 100) all from Alpha Div., Ventron Corp., USA and vanadium nitride (purity 2N, from Materials Research Corp., USA). Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 600h at 1000°C or annealed for 30h at 1500°C in a r.f. furnace under argon (purity: 5N+).

### BINARY SYSTEMS

Phase diagrams for the systems V-Si and V-N are given in [86Mas]. Although not shown in the V-N diagram [86Mas], with varying nitrogen content differently ordered structures occur within the "homogeneity range" of the subnitride  $\beta\text{-V}_2\text{N}_{1-x}$  (tab.16.1). No phase diagram is reported for Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.16.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

The only ternary phase existing in The system V-Si-N is  $\text{V}_5\text{Si}_3\text{N}_{1-x}$  (tab.16.1) which dominates the phase equilibria at 1000°C (fig.16.1 [85Sch]) and 1500°C (fig.16.2 [85Sch]).  $\text{V}_5\text{Si}_3\text{N}_{1-x}$  coexists at 1000°C with  $\text{Si}_3\text{N}_4$ ,  $\text{V}_2\text{N}_{1-x}$  and all binary vanadium silicides stable at this temperature but not with  $\text{VN}_{1-x}$ , silicon or vanadium. [86And] confirms these tie lines except they report  $\text{V}_5\text{Si}_3\text{N}_{1-x}$  to coexist with  $\text{VN}_{1-x}$ . However, thermochemical calculations using the data in tab.16.2 corroborate the experimental findings reported in fig.16.1. Neither  $\text{Si}_3\text{N}_4$  nor  $\text{VN}_{1-x}$  are stable at 1500°C under argon. Thus the tie lines directed from  $\text{VSi}_2$ ,  $\text{V}_5\text{Si}_3\text{N}_{1-x}$  as well as  $\text{V}_2\text{N}_{1-x}$  towards  $\text{Si}_3\text{N}_4$  at 1000°C are

changed toward  $N_2$ (gas) at 1500°C (fig.16.2 [85Sch]). These data confirm earlier reports on the interaction of  $Si_3N_4 + V$  [69Fel],  $Si_3N_4 + VN_{1-x}$  [85Uch],  $VSi_2 + N_2$  [69Fit] and  $V_{0.25}Si_{1.75} + N_2$  [56Now]. Lattice parameters of neither vanadium silicide coexisting with  $V_5Si_3N_{1-x}$ ,  $Si_3N_4$  or  $N_2$ (gas) are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in vanadium silicides.

#### REFERENCES

- [56Now] H.Nowotny, B.Lux and H.Kudielka, "The Behavior of Metal Rich, High Melting Silicides Versus Boron, Carbon, Nitrogen and Oxygen", *Monath.Chem.* 87 (1956) 447-470
- [69Fit] E.Fitzer and K.Reinmuth, Reaction of High Melting Silicides with Nitrogen and Carbon", *Proc 6<sup>th</sup> Int.Plansee Sem.* (Reutte, Austria, 1969) p767-802
- [69Fel] H.Feld, E.Gugel and H.G.Nitzsche, "Silicon Nitride - A Corrosion Resistant High Temperature Material", *Werkstoffe Korros.* 20 (1969) 571-574
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [78Ono] T.Onozuka, "Vacancy Ordering in  $VN_{1-x}$ ", *J.Appl.Cryst.* 11 (1978) 132-136
- [81Smi] J.F.Smith, "The V-Si (Vanadium-Silicon) System", *Bull.Alloy Ph.Diagr.* 2 (1981) 42-48
- [82Ono] T.Onozuka, "Nitrogen Ordering in  $V_5N_4$  and  $V_{22}N_{26}$  Studied by Neutron and Electron Diffraction", *Trans.Jap.Inst.Met.* 23 (1982) 315-319
- [82Pom] R.Pompe, "Some Thermodynamical Properties of the System Vanadium-Nitrogen and Vanadium-Carbon-Nitrogen in the Temperature Range 1000-1550°C", *Thermochim.Acta* 57 (1982) 273-281
- [85Sch] J.C.Schuster and H.Nowotny, "Silicon Nitride and Transition Metals: A Critical Evaluation of Existing Phase Diagram Data Supplemented by New Experimental Results", *Proc.11<sup>th</sup> Int.Plansee Seminar* (Reutte, Austria, 1985) Vol.1, p899-911
- [85Uch] N.Uchida, M.Koizumi and M.Shimada, "Fabrication of  $Si_3N_4$  Ceramics with Metal Nitride Additives by Isostatic Hot Pressing", *J.Amer.Ceram.Soc.* 64 (1981) 549-552
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86And] R.Andruszkiewicz and R.Horyn, "The V-Si-N System at Reduced Nitrogen Pressure", *J.Less Common Met.* 124 (1986) 205-210
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)



Table 16.1: Solid phases in the system V - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
V	cI2 Im $\bar{3}$ m W (A2)	a= 302.71	[85Vil]; powder pattern: ASTM file card # 22-1058
V <sub>3</sub> Si	cP8 Pm $\bar{3}$ n Cr <sub>3</sub> Si (A15)	a= 472.49	[85Vil]; powder pattern: ASTM file card # 19-405
V <sub>3</sub> Si <sub>2</sub>	tI32 I4/mcm Si <sub>3</sub> W <sub>5</sub> (D8 <sub>m</sub> )	a= 942.9 c= 475.6	[85Vil]; powder pattern: ASTM file card # 9-301
V <sub>6</sub> Si <sub>5</sub> (h) T>1160±100	oI44 Ibam Ge <sub>5</sub> Ti <sub>6</sub>	a= 1596.6 b= 750.1 c= 485.8	[85Vil]; powder pattern: ASTM file card # 23-722 27-611
VS <sub>2</sub>	hP9 P6 <sub>3</sub> 22 CrSi <sub>2</sub> (C40)	a= 457.1 c= 637.2	[85Vil]; powder pattern: ASTM file card # 13-260 38-1419
$\beta$ -V <sub>2</sub> N <sub>1-x</sub> phases:			
V <sub>2</sub> N <sub>4</sub>	hP* P6 <sub>3</sub> 22 V <sub>2</sub> N <sub>4</sub>	a= 491.0 c= 455	[82Ono]; powder pattern given
V <sub>2</sub> N	hP9 P $\bar{3}$ 1m V <sub>2</sub> N	a= 491.7 c= 456.8	[85Vil]; powder pattern: ASTM file card # 6-624 30-1420, 32-1413, 33-1439
V <sub>32</sub> N <sub>26</sub> T<500	tP58 P4 <sub>2</sub> /nmc V <sub>32</sub> N <sub>26</sub>	a= 2a <sub>VN</sub> c= 2a <sub>VN</sub>	[78Ono]; powder pattern given
VN <sub>1-x</sub>	cF8 Fm $\bar{3}$ m NaCl (B1)	a= 413.6	[85Vil]; powder pattern: ASTM file card # 25-1252 35-768
Si	cF8 Fd $\bar{3}$ m C (A4)	a= 357.0 c= 357.0	[85Vil]; powder pattern: ASTM file card # 5-565

Tab.16.1 continued

$\alpha$ - $\text{Si}_3\text{N}_4$	hP28	a= 781.8	[85Vil]; powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	$\text{Si}_3\text{N}_4$		
$\beta$ - $\text{Si}_3\text{N}_4$	hP14	a= 760.8	[85Vil]; powder pattern:
	$\text{P6}_2/\text{m}$	c= 291.1	ASTM file card # 29-1132
	$\text{Si}_3\text{N}_4$		33-1160
$*\text{V}_x\text{Si}_{1-x}\text{N}_{1-x}$	hP18	a= 715.54	[85Sch]; powder pattern:
	$\text{P6}_2/\text{mcm}$	c= 485.21	ASTM file card # 8-379
	filled $\text{Mn}_2\text{Si}_3$		

Tab.16.2: Thermodynamic data for the solid phases in V - Si - N

phase	$\Delta G_f^\circ$ (J/gramatom)	Comment
.1429 $\text{Si}_3\text{N}_4$	-124602 + 57.95 T	[76Fro]
.3333 $\text{VSi}_2$	-40700 + 3.15 T	[81Smi]
.0909 $\text{V}_2\text{Si}_3$	-49600 + 3.1 T	[81Smi]
.1250 $\text{V}_2\text{Si}_3$	-53800 + 4.1 T	[81Smi]
.2500 $\text{V}_2\text{Si}_3$	-43100 + 3.33 T	[81Smi]
V(s.s.10at% N)	-11175 (at 1773K)	estimated from plot $\Delta G_f^{1773}$ vs. $x_N$
V(s.s.5at% N)	-8000 (at 1273K)	estimated from plot $\Delta G_f^{1273}$ vs. $x_N$
.3431 $\text{V}_2\text{N}_{0.2}$	-89591 + 30.55 T	[76Fro]
.5000 $\text{VN}_{1-x}$	-77404 + 46.024 T	[82Pom]

**Fig.16.1: Isothermal section observed in the system V - Si - N  
at 1000°C (in the absence of external nitrogen pressure)**

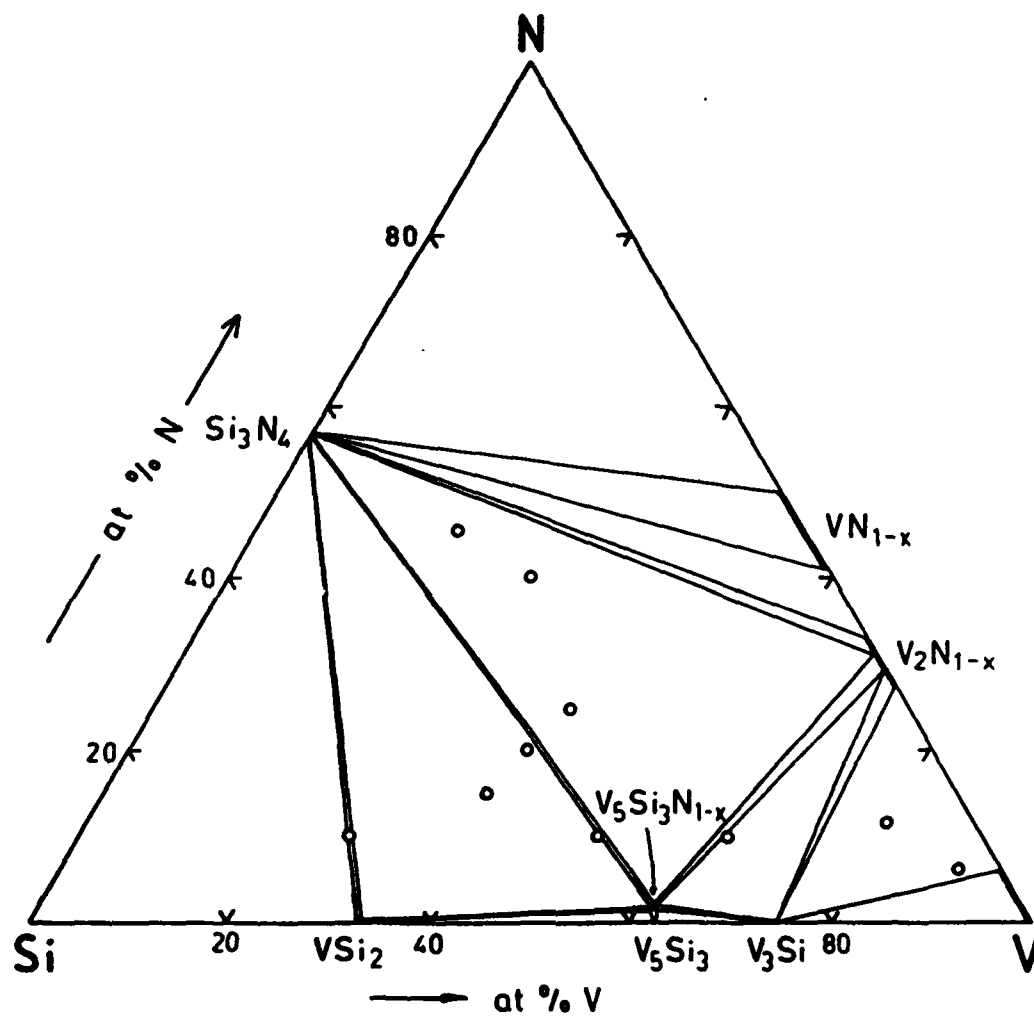
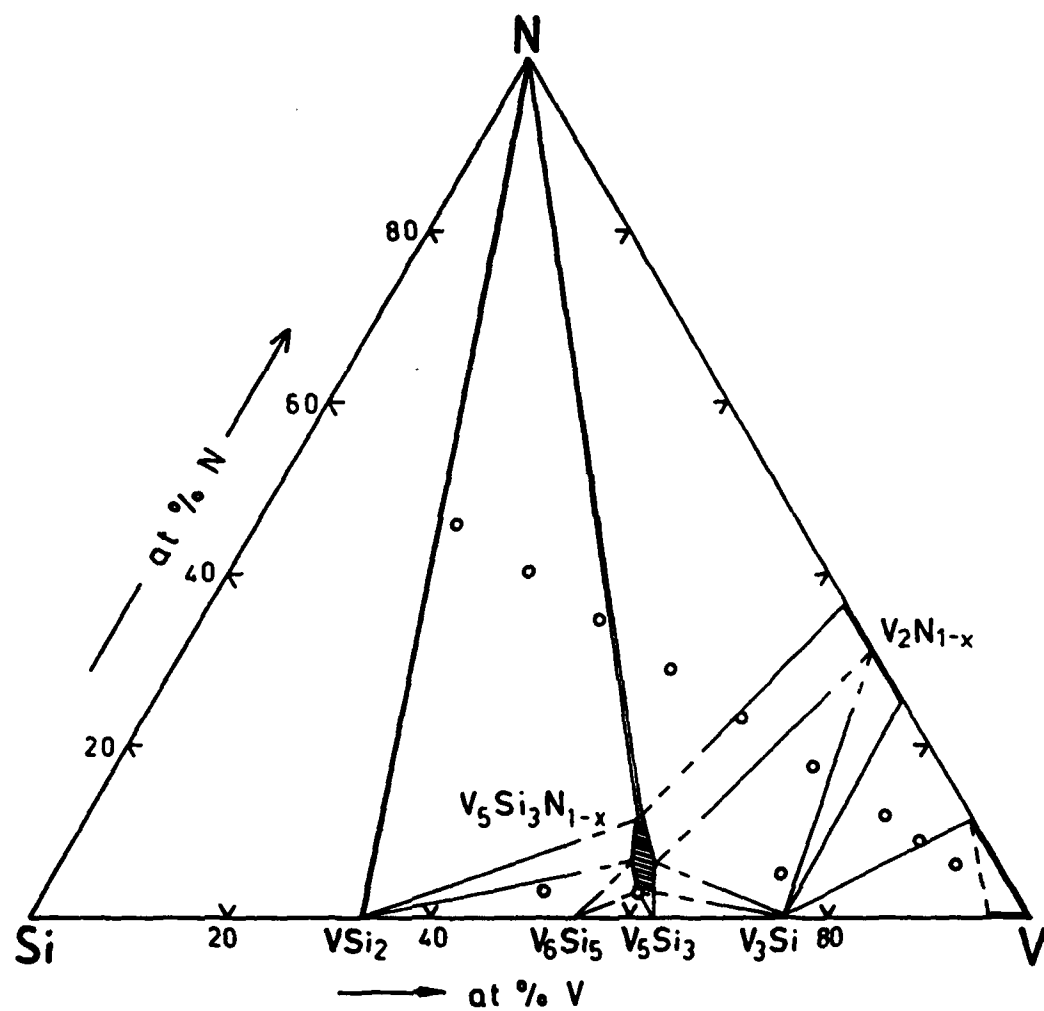


Fig.16.2: Isothermal section observed in the system V - Si - N  
at 1500°C (under argon)



## SYSTEM NIOBIUM - SILICON - NITROGEN (Nb-Si-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria of Nb-Si-N between 1000°C and 1500°C were determined by x-ray analysis [85-1Sch]. The alloys investigated were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si), silicon (purity: 3N), niobium (purity: 2N8; impurities in ppm: Ta 800, Ti 100, Fe 80, O 80, C 50, W 50, other < 10) and niobium nitride ( $\delta\text{-NbN}$ , purity: 3N) all from Alpha Div., Ventron Corp., USA. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 600h at 1000°C or annealed for 30h at 1500°C in a r.f. furnace under argon (purity: 5N+).

### BINARY SYSTEMS

The phase diagram of [80Koc] for the system Nb-Si (fig.17.1) is preferred to the diagram given in [86Mas], because it shows in detail the stability ranges of the two modifications of  $\text{Nb}_3\text{Si}_2$  (tab.17.1). The phase diagram for the system Nb-N (fig.17.2 [85-2Sch]) is based on [83Bra] as well as on the compilation by [79Pol]. Phases stable only at nitrogen partial pressures higher than  $10^5$  Pa [71Ter] are not included in this figure. No phase diagram is reported for Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.17.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

The only ternary phase existing in the system Nb-Si-N is  $\text{Nb}_3\text{Si}_2\text{N}_{1-x}$  (tab.17.1).  $\text{Nb}_3\text{Si}_2\text{N}_{1-x}$  dominates the phase equilibria in the isothermal section at 1500°C (fig.17.3 [85-1Sch]) but does not occur at 1000°C (fig.17.4 [85-1Sch]). At this temperature  $\text{Si}_3\text{N}_4$  coexist with  $\epsilon\text{-NbN}$ ,  $\gamma\text{-Nb}_3\text{N}_2$ ,  $\beta\text{-Nb}_3\text{N}_2$ ,  $\text{Nb}_3\text{Si}_2$  and  $\text{NbSi}_2$  but not with niobium. These data confirm reports on the interaction of  $\text{Si}_3\text{N}_4$  + Nb or niobium compounds [56Bre][76Kri][85Uch][86Sug] as well as on the reactions of niobium

silicides with  $N_2$ (gas) [56Now][69Fit]. Lattice parameters of neither niobium silicide coexisting with  $Nb_2Si_3N_{1-x}$ ,  $\beta-Nb_2N$ ,  $Si_3N_4$  or  $N_2$ (gas) are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in niobium silicides.

Only limited thermodynamic data are available for binary niobium silicides (tab.17.2). These are not sufficient to allow calculation of tie lines to be compared with the experimentally observed equilibria. However, it is evident, that there is no pressure or temperature range where  $Si_3N_4$  coexists in equilibrium with niobium.

## REFERENCES

- [56Bre] L. Brewer and O. Krikorian, "Reactions of Refractory Silicides with Carbon and Nitrogen", *J. Electrochem. Soc.* 103 (1956) 38-50
- [56Now] H. Nowotny, B. Lux and H. Kudielka, "The Behavior of Metal Rich, High Melting Silicides Versus Boron, Carbon, Nitrogen and Oxygen", *Monath. Chem.* 87 (1956) 447-470
- [69Fit] E. Fitzner and K. Reinmuth, Reaction of High Melting Silicides with Nitrogen and Carbon", *Proc 6<sup>th</sup> Int. Plansee Sem.* (Reutte, Austria, 1969) p767-802
- [71Ter] N. Terao, "New Phases of Niobium Nitride", *J. Less Common Met.* 23 (1971) 159-169
- [73Cha] T. Chart, "Thermochemical Data for Transition Metal-Silicon Systems", *High Temp. High Press.* 5 (1973) 241-252
- [76Kri] Y. I. Krilov and V. A. Bronnikov, "Thermit Mixtures on the Basis of Exothermal Reactions of BN and  $Si_3N_4$  with Metals", *Poroshk. Met.* (1) (1976) 52-55
- [76Pro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [79Pol] C. Politis, "Phase Relationships in the Nb-N and Ta-N Systems", Report KfK 2881 (Kernforschungszentrum Karlsruhe, FRG, 1979) p126-128
- [80Koc] Y. A. Kochershinskii, L. M. Yupko and E. A. Shishkin, "The Nb-Si Phase Diagram", *Izv. Akad. Nauk SSSR, Met.* (1) (1980) 205-211
- [83Bra] G. Brauer and W. Kern, "Decomposition Pressures and Phase Limits of Niobium Nitrides", *Z. Anorg. Allg. Chem.* 507 (1983) 127-141
- [85-1Sch] J. C. Schuster and H. Nowotny, "Silicon Nitride and Transition Metals: A Critical Evaluation of Existing Phase Diagram Data Supplemented by New Experimental Results", *Proc. 11<sup>th</sup> Int. Plansee Seminar* (Reutte, Austria, 1985) Vol. 1, p899-911
- [85-2Sch] J. C. Schuster in "Boron Nitride and Silicon Nitride Systems", 1<sup>st</sup> Semiannual Report to the European Research Office of the USA under contract DAJA84-C-0038 (1985)
- [85Uch] N. Uchida, M. Koizumi and M. Shimada, "Fabrication of  $Si_3N_4$  Ceramics with Metal Nitride Additives by Isostatic Hot Pressing", *J. Amer. Ceram. Soc.* 64 (1981) 549-552
- [85Vil] P. Villars and L. D. Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, OH., 1985)
- [86Mas] T. B. Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer. Soc. Met., Metals Park, OH., 1986)
- [86Sug] K. Suganuma, T. Okamoto, Y. Miyamoto, M. Shimada and M. Koizumi, "Joining  $Si_3N_4$  to Type 405 Steel with Soft Metal Interlayers", *Mater. Sci. Technol.* 2 (1986) 1156-1161

Table 17.1: Solid phases in the system Nb - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Nb	cI2 Im $\bar{3}$ m W (A2)	a= 330.02	[85Vil]; powder pattern: ASTM file card # 34-370
Nb <sub>3</sub> Si	tP32 P4 <sub>2</sub> /n T <sub>1</sub> P	a= 1022.4 c= 518.9	[85Vil]; powder pattern: ASTM file card # 22-763
Nb <sub>3</sub> Si <sub>2</sub> (r) T<1940	tI32 I4/mcm Cr <sub>2</sub> B <sub>3</sub> (D8 <sub>1</sub> )	a= 657.0 c= 1188.4	[85Vil]; powder pattern: ASTM file card # 30-874
Nb <sub>3</sub> Si <sub>2</sub> (h) T>1650	tI32 I4/mcm Si <sub>3</sub> W <sub>5</sub> (D8 <sub>m</sub> )	a= 1002.6 c= 507.17	[85Vil]; powder pattern: ASTM file card # 30-875
NbSi <sub>2</sub>	hP9 P6 <sub>2</sub> 22 CrSi <sub>2</sub> (C40)	a= 481.9 c= 659.2	[85Vil]; powder pattern: ASTM file card # 8-450
$\beta$ -Nb <sub>2</sub> N	hP9 P $\bar{3}$ 1m V <sub>2</sub> N	a= 526.7 c= 498.8	[85Vil]; powder pattern: ASTM file card # 30-869
$\gamma$ -Nb <sub>4</sub> N <sub>3</sub>	tI14 I4/mmm Nb <sub>4</sub> N <sub>3</sub>	a= 438.2 c= 863.2	[85Vil]; powder pattern: ASTM file card # 20-803
$\delta$ -NbN <sub>1-x</sub> (h)	cF8 Fm $\bar{3}$ m NaCl (B1)	a= 439.4	[85Vil]; powder pattern: ASTM file card # 25-1361 34-337, 38-1155
$\epsilon$ -NbN	hP8 P6 <sub>3</sub> /mmc TiAs	a= 295.8 c= 1127.3	[85Vil]; powder pattern: ASTM file card # 20-801
Nb <sub>3</sub> N <sub>6</sub>	hP22 P6 <sub>3</sub> /mcm Nb <sub>3</sub> N <sub>6</sub>	a= 519.3 c= 1038.0	[85Vil]; powder pattern: given in [71Ter]



Tab.17.1 continued

$\text{Nb}_3\text{N}_5$	tI18	a= 687.3	[85Vil]; powder pattern: given in [71Ter]
	I4/m	c= 429.8	
Si	RhLi <sub>4</sub> H <sub>4</sub>		
	cF8	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
	Fd $\bar{3}$ m		
	C (A4)		
$\alpha\text{-Si}_3\text{N}_4$	hP28	a= 781.8	[85Vil]; powder pattern: ASTM file card # 9-250
	P31c	c= 559.1	
	$\text{Si}_3\text{N}_4$		
$\beta\text{-Si}_3\text{N}_4$	hP14	a= 760.8	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160
	P6 <sub>3</sub> /m	c= 291.1	
	$\text{Si}_3\text{N}_4$		
* $\text{Nb}_3\text{Si}_3\text{N}_{1-x}$ T>1000	hP18	a= 751.69	[85-1Sch]; powder pattern: ASTM file card # 8-422
	P6 <sub>3</sub> /mcm filled $\text{Mn}_3\text{Si}_3$	c= 531.03	

Tab.17.2: Thermodynamic data for the solid phases in Nb - Si - N

phase	$\Delta G_f^\circ$ (J/gramatom)	Comment
.1429 $\text{Si}_3\text{N}_4$	$-124602 + 57.95 T$	[76Fro]
.3333 $\text{NbSi}_2$	$\Delta H_f^{298} = -46000$	[73Cha]
.1250 $\text{Nb}_2\text{Si}_3$	$\Delta H_f^{298} = -60700$	[73Cha]
.2500 $\text{Nb}_2\text{Si}$		
.3333 $\text{Nb}_2\text{N}$	$-90793 + 30.96 T$	[76Fro]

Fig.17.1: Phase diagram of the boundary system niobium - silicon

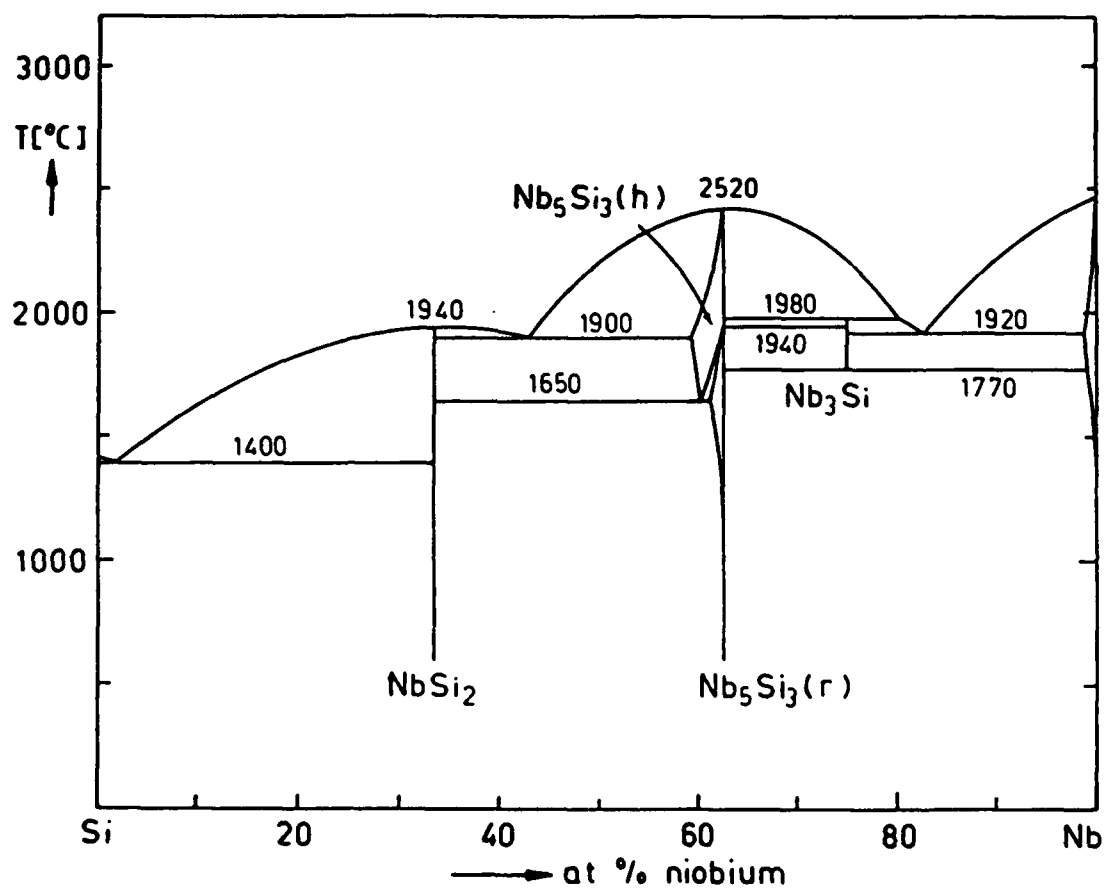
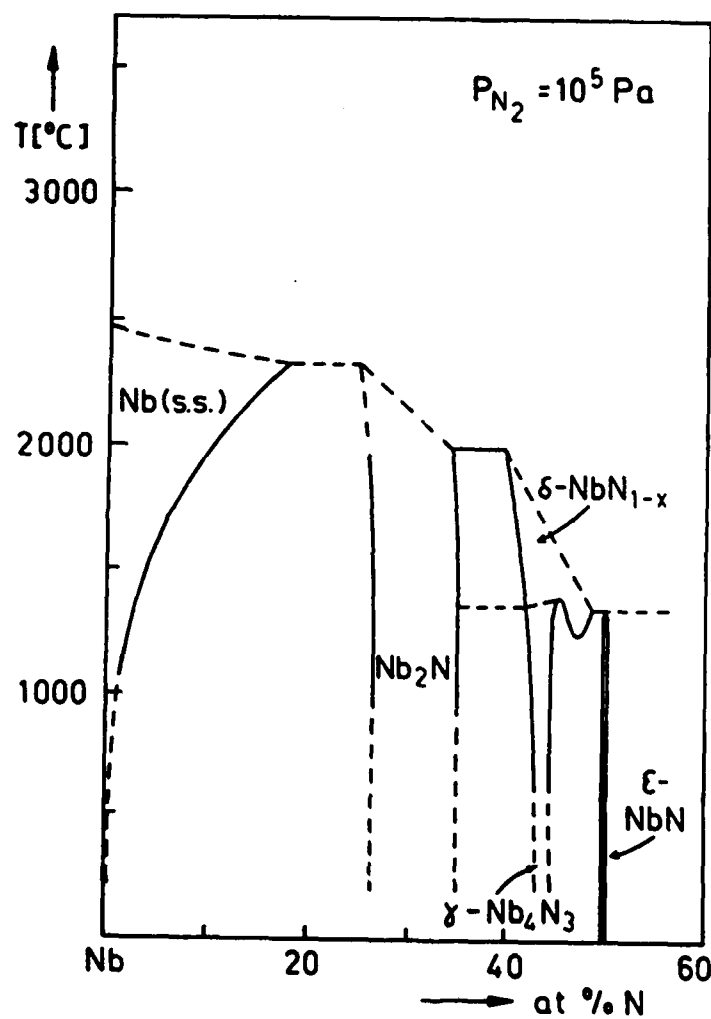


Fig.17.2: Phase diagram of the boundary system niobium - nitrogen



**Fig.17.3: Isothermal section observed in the system Nb - Si - N at 1000°C (in the absence of external nitrogen pressure)**

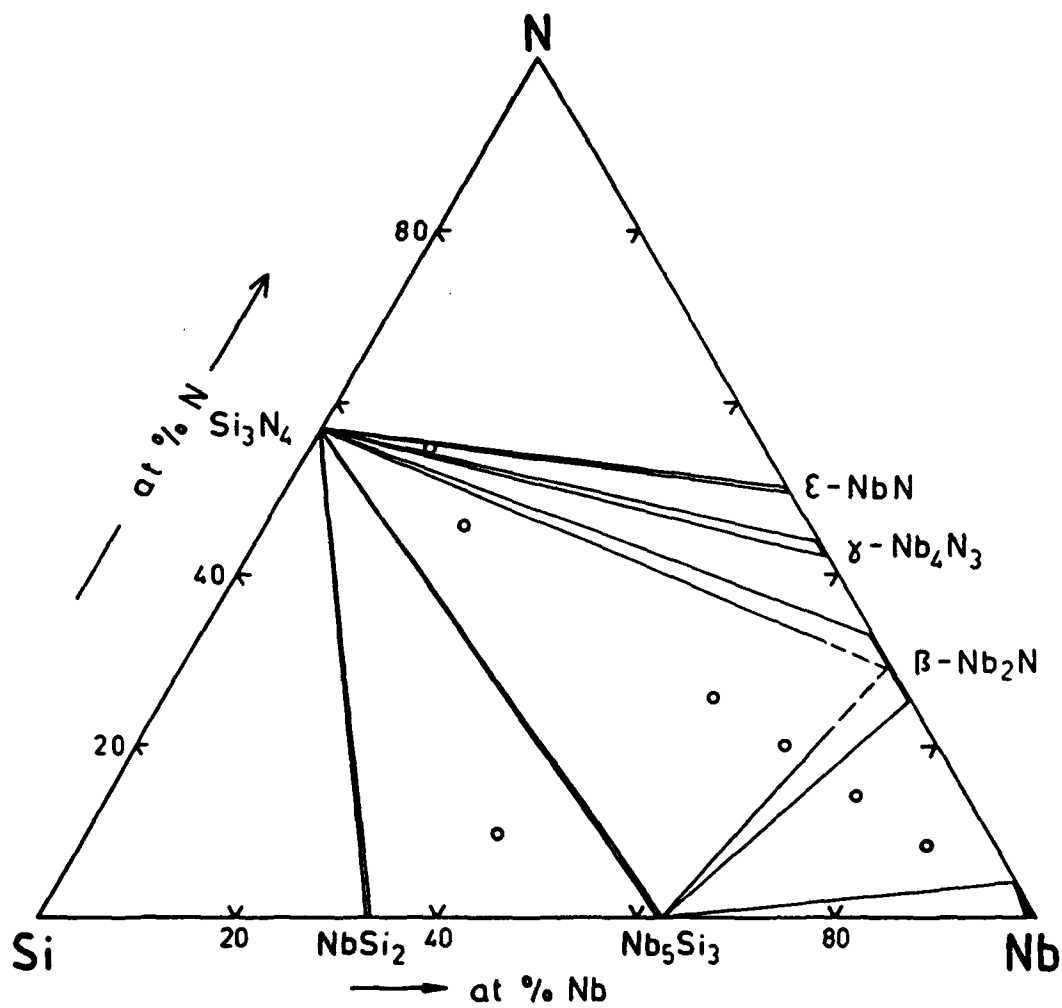
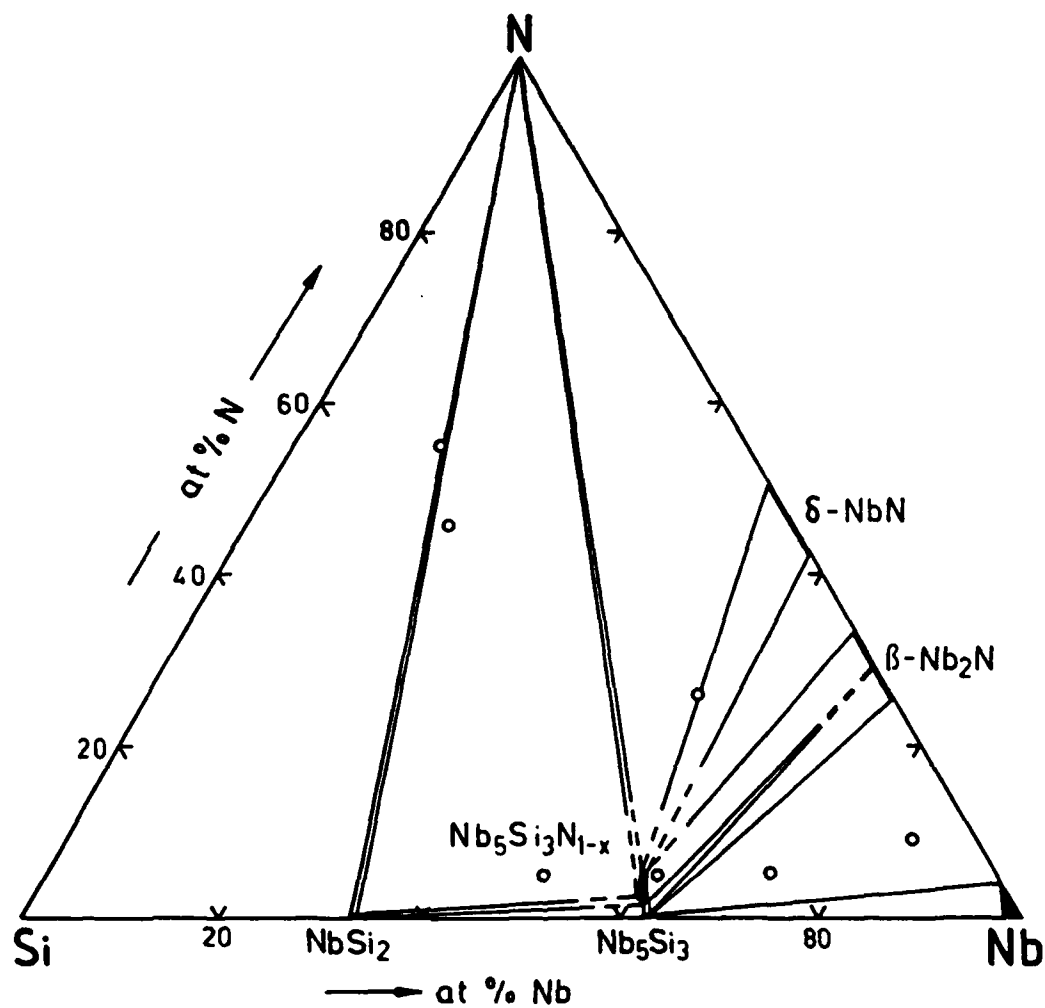


Fig.17.4: Isothermal section observed in the system Nb - Si - N  
at 1500°C (under argon)



## SYSTEM TANTALUM - SILICON - NITROGEN (Ta-Si-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria of Ta-Si-N between 1000°C and 1500°C were determined by x-ray analysis [56Bre],[85Sch]. The alloys investigated in the latter work were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si), silicon (purity: 3N) and tantalum (purity: 3N6; impurities in ppm: O 1700, Fe 150, Nb 100, other < 10) all from Alpha Div., Ventron Corp., USA. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 600h at 1000°C or annealed for 30h at 1500°C in a r.f. furnace under argon (purity: 5N+).

### BINARY SYSTEMS

The tantalum-silicon phase diagram of [81Koc] (fig.18.1, thermodynamically modelled by [89Vah]) is preferred over the diagram given in [86Mas]. Five intermediate phases exist (tab.18.1). The phase diagram for the system Ta-N (fig.18.2) is based on [83Ett] and supplemented by original information taken from [69Boo],[73Gei],[75Gat] and [84Koy]. No phase diagram is reported for the system Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.18.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

The only ternary phase existing in the system Ta-Si-N is  $\text{Ta}_3\text{Si}_2\text{N}_{1-x}$  (tab.18.1).  $\text{Ta}_3\text{Si}_2\text{N}_{1-x}$  dominates the phase equilibria in the isothermal section at 1500°C under argon (fig.18.3 [85Sch]) and 1327°C under nitrogen (fig.18.4 [56Bre]) but does not occur at 1000°C (fig.18.5 [85Sch]). At the latter temperature  $\text{Si}_3\text{N}_4$  coexist with  $\epsilon\text{-Ta}_3\text{N}_5$ ,  $\beta\text{-Ta}_2\text{N}$ ,  $\text{Ta}_3\text{Si}_2$  and  $\text{TaSi}_2$ , but not with  $\text{Ta}_2\text{Si}$ ,  $\text{Ta}_3\text{Si}$  or tantalum. These data confirm reports on the interaction of  $\text{Si}_3\text{N}_4$  + Ta or TaN [81Tam][85Uch] as well as on the reactions of tantalum silicides with  $\text{N}_2$ (gas) [56Now]

[69Fit]. Lattice parameters of neither tantalum silicide coexisting with  $Ta_3Si_2N_{1-x}$ ,  $\beta-Ta_2N$ ,  $Si_3N_4$  or  $N_2$  (gas) are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in tantalum silicides.

Using the thermodynamic data in tab.18.2 for the calculation of tie lines, the experimental results at 1000°C (fig.18.3) are corroborated. There is no pressure or temperature range where  $Si_3N_4$  coexists in equilibrium with tantalum.

#### REFERENCES

- [53Now] H. Nowotny, H. Schachner, R. Kieffer and F. Benesovsky, "X-Ray Investigation of the System Tantalum-Silicon", *Monatsh. Chem.* 84 (1953) 1-12
- [56Bre] L. Brewer and O. Krikorian, "Reactions of Refractory Silicides with Carbon and Nitrogen", *J. Electrochem. Soc.* 103 (1956) 38-50
- [56Now] H. Nowotny, B. Lux and H. Kudielka, "The Behavior of Metal Rich, High Melting Silicides Versus Boron, Carbon, Nitrogen and Oxygen", *Monatsh. Chem.* 87 (1956) 447-470
- [69Fit] E. Fitzer and K. Reinmuth, "Reaction of High Melting Silicides with Nitrogen and Carbon", *Proc 6<sup>th</sup> Int. Plansee Sem.* (Reutte, Austria, 1969) p767-802
- [69Boo] P. H. Booker and C. E. Brukl, Report AFML-TR-69-117, Part VI (Wright-Patterson AFB, OH, USA, 1969)
- [71Ter] N. Terao, "Structures of Tantalum Nitrides" *Jap. J. Appl. Phys.* 10 (1971) 248-259
- [73Gei] R. H. Geils and D. I. Potter, "Phase Equilibria in the Metal Rich Side of the Ta-N System", *Met. Trans.* 4 (1973) 1469-1474
- [75Gat] J. Gatterer, G. Dufek, P. Ettmayer and R. Kieffer, "The Cubic Tantalum Mononitride (B1-Type) and the Solid Solutions with Isotypic Transition Metal Nitrides and Carbides", *Monatsh. Chem.* 106 (1975) 1137-1147
- [76Pro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [81Koc] Y. A. Kochershinskii, O. A. Kulik and E. A. Shishkin, "The Phase Diagram of the System Tantalum-Silicon", *Doklady Akad. Nauk SSSR* 261 (1981) 106-108
- [81Tam] N. Tamari and Y. Toibana, "Reaction Between Silicon Nitride and Tantalum Metal at High Temperature", *Osaka Kogyo Gijutsu Shikensho Kiho* 32 (1981) 126-129
- [83Ett] P. Ettmayer and A. Vendl, "Phase Equilibria and Crystal Structures of Transition Metal Nitrides", in "The Science of Hard Materials" edited by R. K. Viswanadham, D. J. Rowcliffe and J. Gurland (Plenum Press, New York, 1983) p47-63

- [84Koy] T.Koyama, N.Kieda, K.Uematsu, N.Mizutani and M.Kato, "Phase Relation of Ta-N System", *Yogyo Kyokai Shi* 92 (1984) 255-260
- [85Sch] J.C.Schuster and H.Nowotny, "Silicon Nitride and Transition Metals: A Critical Evaluation of Existing Phase Diagram Data Supplemented by New Experimental Results", *Proc. 11<sup>th</sup> Int. Plansee Seminar* (Reutte, Austria, 1985) Vol.1, p899-911
- [85Uch] N.Uchida, M.Koizumi and M.Shimada, "Fabrication of  $Si_3N_4$  Ceramics with Metal Nitride Additives by Isostatic Hot Pressing", *J.Amer. Ceram.Soc.* 64 (1981) 549-552
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [89Vah] C.Vahlas, P.Y.Chevalier and E.Blanquet, "A Thermodynamic Evaluation of Four Si-M (M=Mo, Ta, Ti, W) Binary Systems", *CALPHAD* 13 (1989) 273-292



Table 18.1: Solid phases in the system Ta - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Ta	cI2 Im $\bar{3}$ m W (A2)	a= 330.25	[85Vil]; powder pattern: ASTM file card # 4-788
Ta <sub>3</sub> Si	tP32 P4 <sub>2</sub> /n T <sub>1</sub> P	a= 1019.3 c= 517.5	[85Vil]; powder pattern: ASTM file card # 18-1312
Ta <sub>2</sub> Si	tI12 I4/mcm Al <sub>2</sub> Cu (C16)	a= 616 c= 505.6	[53Now]; powder pattern: ASTM file card # 6-552
Ta <sub>3</sub> Si <sub>2</sub> (r) T<2160	tI32 I4/mcm Cr <sub>2</sub> B <sub>2</sub> (D8 <sub>1</sub> )	a= 651.6 c= 1187.3	[85Vil]; powder pattern: ASTM file card # 9-232
Ta <sub>3</sub> Si <sub>2</sub> (h) T>2160	tI32 I4/mcm Si <sub>3</sub> W <sub>5</sub> (D8 <sub>m</sub> )	a= 988 c= 506	[85Vil]; powder pattern: ASTM file card # 9-280
TaSi <sub>2</sub>	hP9 P6 <sub>2</sub> 22 CrSi <sub>2</sub> (C40)	a= 478.21 c= 656.95	[85Vil]; powder pattern: ASTM file card # 8-53 38-483
Ta <sub>3</sub> N <sub>2</sub> (r) T<790	c**	a= 1010	[85Vil]
$\beta$ -Ta <sub>2</sub> N (r) T<1850	hP9 P $\bar{3}$ 1m V <sub>2</sub> N	a= 528.5 c= 491.9	[85Vil]; powder pattern: ASTM file card # 31-1370
$\beta$ -Ta <sub>2</sub> N (h) T>1650	hP3 P6 <sub>3</sub> /mmc Fe <sub>2</sub> N (L'3)	a= 304.76 c= 491.87	[85Vil]; powder pattern: ASTM file card # 26-985
$\delta$ -TaN <sub>1-x</sub> (h) T>1750	cF8 Fm $\bar{3}$ m NaCl (B1)	a= 433	[85Vil]; powder pattern: ASTM file card # 32-1283

Tab.18.1 continued

$\epsilon$ -TaN	hP6	a= 519.6	[85Vil]; powder pattern:
T<1950	P6 <sub>2</sub> m	c= 291.1	ASTM file card # 9-257
	TaN		
Ta <sub>3</sub> N <sub>6</sub>	hP22	a= 516	[85Vil]; powder pattern:
	P6 <sub>3</sub> /mnc	c= 1027	given in [71Ter]
	Nb <sub>3</sub> N <sub>6</sub>		
Ta <sub>3</sub> N <sub>5</sub>	tI18	a= 683.1	[85Vil]; powder pattern:
	I4/m	c= 426.9	given in [71Ter]
	RhLi <sub>3</sub> N <sub>4</sub>		
Si	cF8	a= 542.86	[85Vil]; powder pattern:
	Fd3m		ASTM file card # 5-565
	C (A4)		
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28	a= 781.8	[85Vil]; powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si <sub>3</sub> N <sub>4</sub>		
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14	a= 760.8	[85Vil]; powder pattern:
	P6 <sub>3</sub> /m	c= 291.1	ASTM file card # 29-1132
	Si <sub>3</sub> N <sub>4</sub>		33-1160
*Ta <sub>3</sub> Si <sub>2</sub> N <sub>1-x</sub>	hP18	a= 750.88	[85Sch]; powder pattern:
T> 1000	P6 <sub>3</sub> /mcm	c= 524.57	ASTM file card # 6-594
	filled Mn <sub>3</sub> Si <sub>3</sub>		

Tab.18.2: Thermodynamic data for the solid phases in Ta - Si - N

phase	$\Delta G_f^\circ$ (J/gramatom)	Comment
.1429 $\text{Si}_3\text{N}_4$	$-124602 + 57.95 \text{ T}$	[76Fro]
.3333 $\text{TaSi}_2$	$-39700 + 5.084 \text{ T}$	[89Vah]
.1250 $\text{Ta}_3\text{Si}_2$	$-41800 + 5.599 \text{ T}$	[89Vah]
.3333 $\text{Ta}_2\text{Si}$	$-41800 + 6.391 \text{ T}$	[89Vah]
.2500 $\text{Ta}_2\text{Si}$	$-38700 + 7.331 \text{ T}$	[89Vah]
.3333 $\text{Ta}_2\text{N}$	$-67920 + 17.015 \text{ T}$	[76Fro]

Fig.18.1: Phase diagram of the boundary system tantalum - silicon

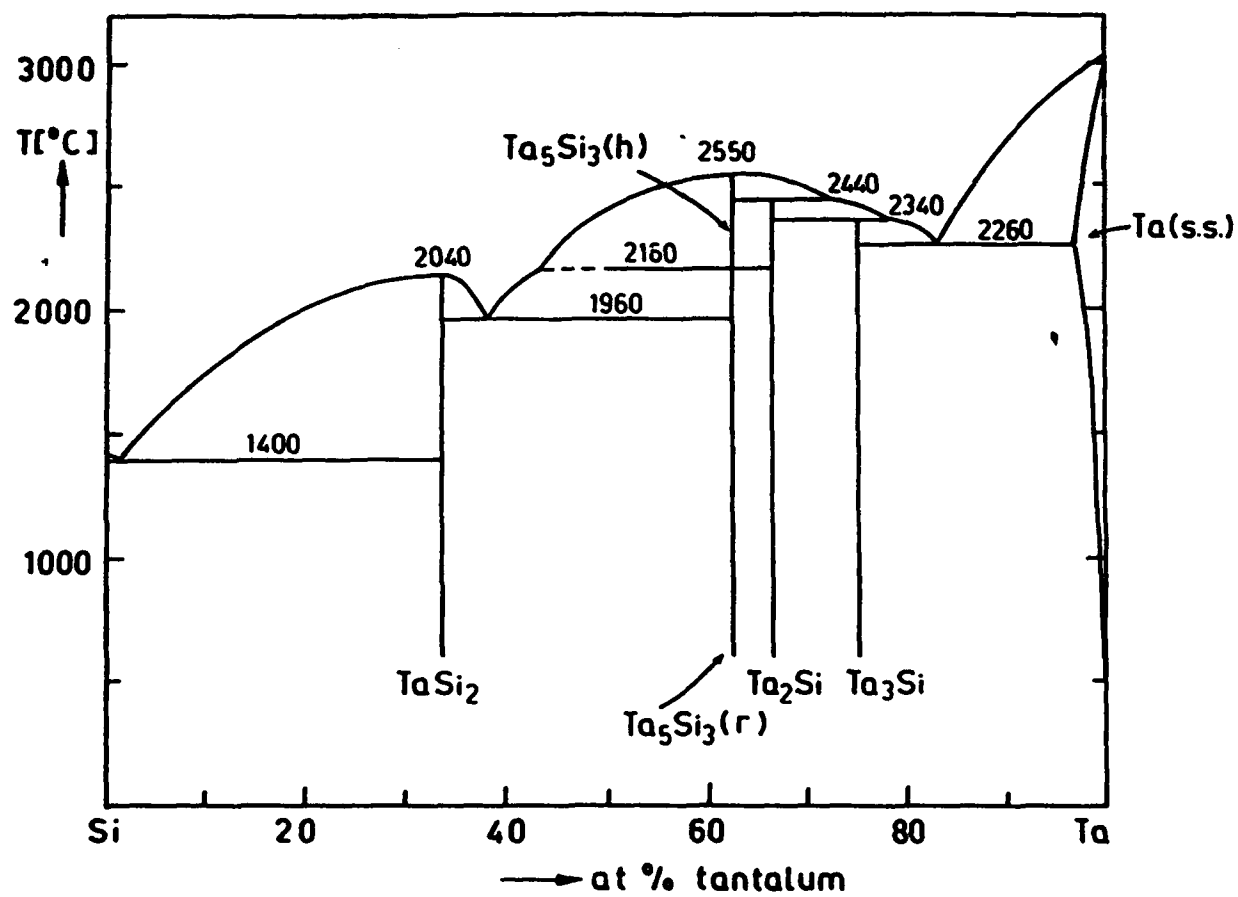


Fig.18.2: Phase diagram of the boundary system tantalum - nitrogen

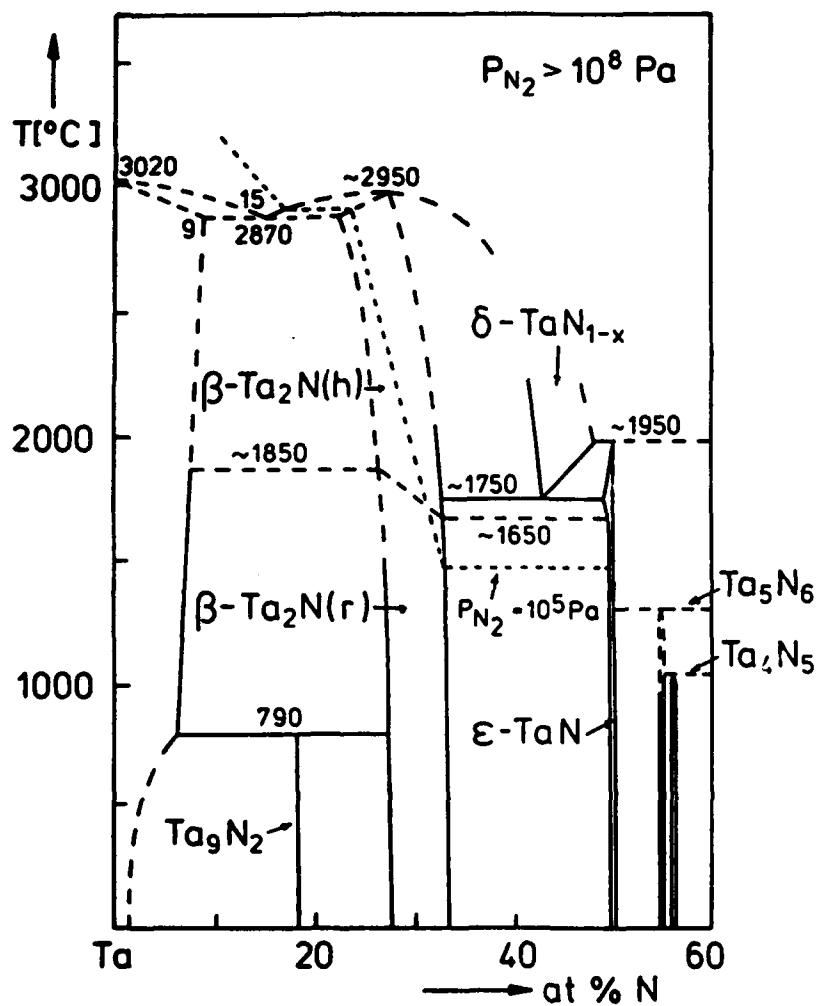


Fig.18.3: Isothermal section observed in the system Ta - Si - N  
at 1000°C (in the absence of external nitrogen pressure)

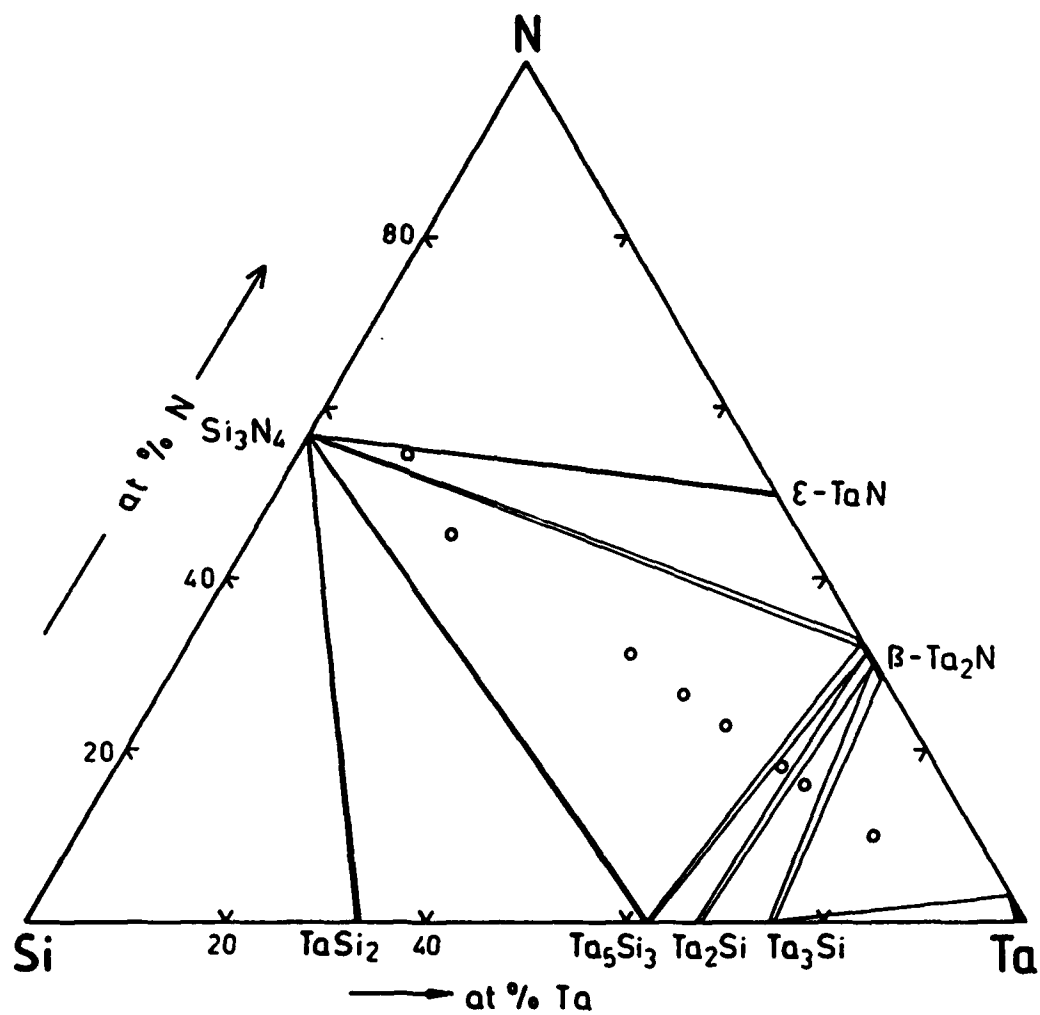


Fig.18.4: Isothermal section observed in the system Ta - Si - N  
at 1327°C (under nitrogen)

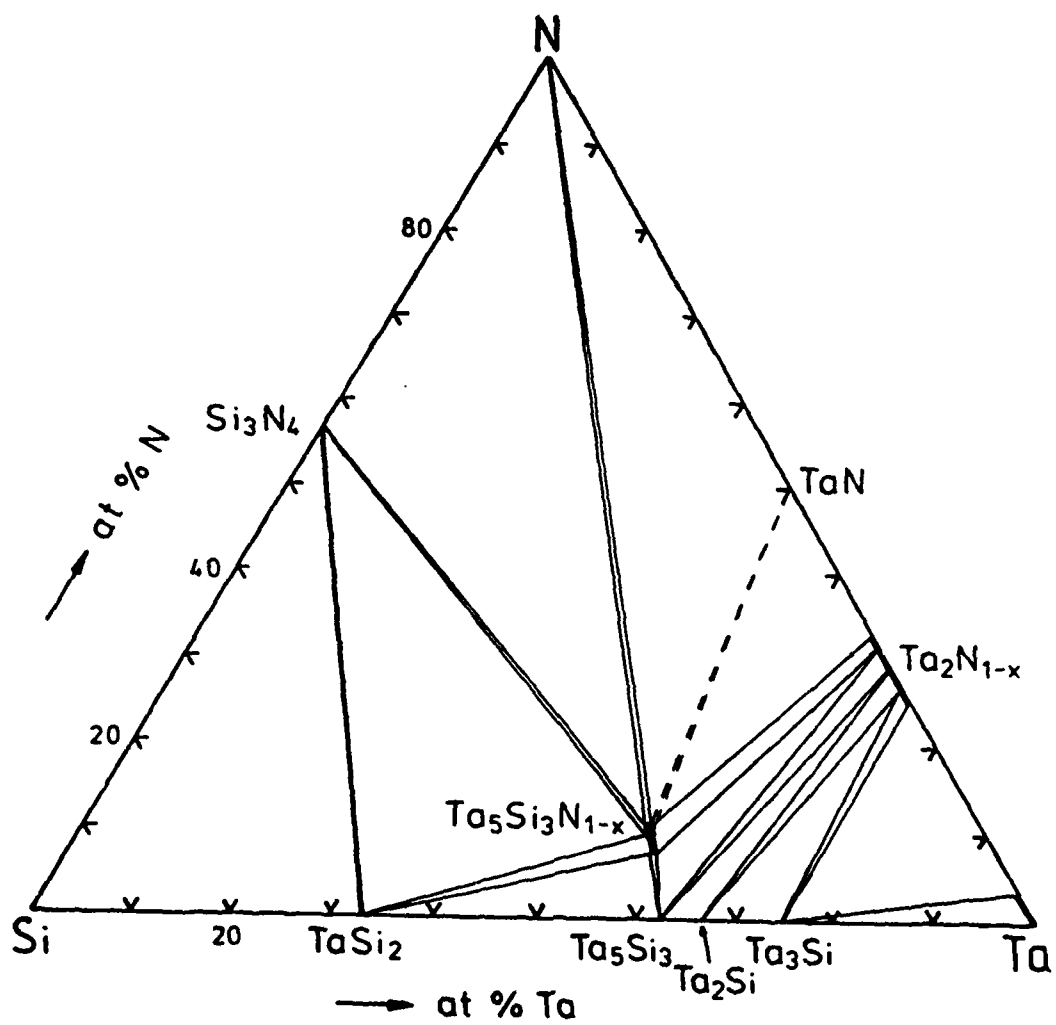
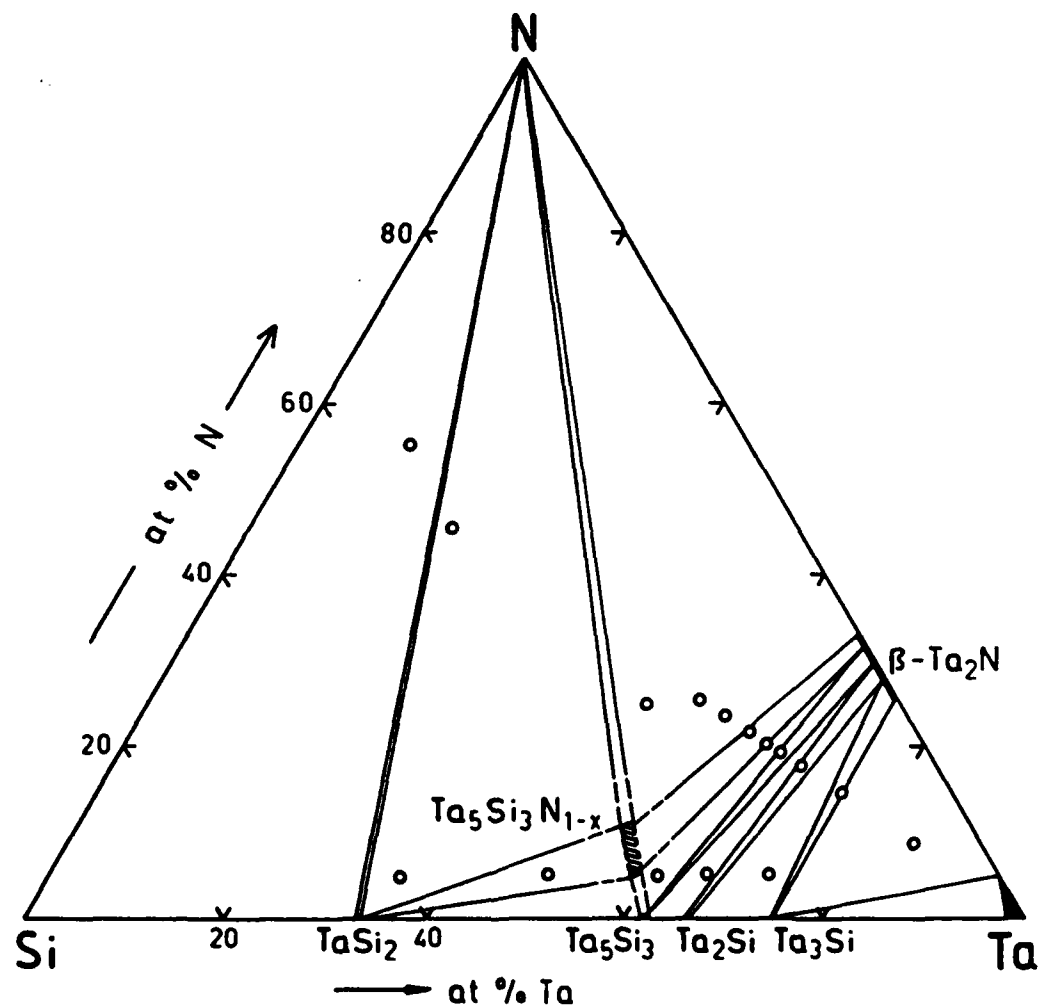


Fig.18.5: Isothermal section observed in the system Ta - Si - N  
at 1500°C (under argon)





## INTRODUCTION / EXPERIMENTAL

Phase equilibria of Cr-Si-N between 1000°C and 1600°C were determined by x-ray analysis [81Kat],[88Sch]. The alloys investigated in the latter work were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si), silicon (purity: 3N) and chromium (purity: 3N5) all from Alpha Div., Ventron Corp., USA. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 400h at temperatures up to 1000°C or annealed in an r.f. furnace under argon (purity: 5N+) at temperatures up to 1400°C.

## BINARY SYSTEMS

In the binary system Cr-Si [86Mas] four intermediate phases exist (tab.19.1). The phase diagram of Cr-N (fig.19.1) is due to [71Sve] (reproduced e.g. in [76Mof] and [81Kat]) but modified according to [76Fro]. At 1000°C and  $p(\text{N}_2) = 10^5 \text{ Pa}$  (tab.19.1) two intermediate phases,  $\text{Cr}_2\text{N}$  and  $\text{CrN}$ , exist. However neither phase is stable at this temperature and  $p(\text{N}_2) \leq 70 \text{ Pa}$  [76Fro],[81Yam]. No phase diagram is reported for Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.19.1). The solubility of nitrogen in silicon as well as in chromium is very low [76Fro].

## SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Cr-Si-N (tab.19.1). Four experimentally determined isothermal sections are reported [81Kat],[88Sch]: At 1000°C as well as 1400°C in the absence of external nitrogen pressure (figs.19.2 and 19.4 resp.); at 1000°C under  $p(\text{N}_2)$  exceeding  $\approx 40 \text{ Pa}$  (fig.19.3); and at 1600°C at  $p(\text{N}_2) = 10^5 \text{ Pa}$  (fig.19.5). These data confirm earlier reports on the decomposition of  $\text{Si}_3\text{N}_4$  in contact with chromium at temperatures of 900°C and above [56Now],[66Mue],

[69Fel],[73Cha],[76Kri],[77Kha],[83Ore],[89Got].The silicide most rich in chromium coexisting with  $\text{Si}_3\text{N}_4$  is  $\text{Cr}_3\text{Si}$  at 1000°C and  $\text{Cr}_5\text{Si}_3$  at 1400°C and 1600°C.Lattice parameters of neither chromium silicide coexisting with  $\text{Si}_3\text{N}_4$  or  $\text{N}_2$  gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in chromium silicides.

Using the thermodynamic data in tab.19.2 the nitrogen pressures for the invariant equilibria occurring at 1000°C as well as at 1400°C are calculated (tab.19.3).The resulting tie lines are consistent with the experimentally observed isothermal sections (figs.19.2 to 19.4).There is no pressure or temperature range where  $\text{Si}_3\text{N}_4$  coexists in equilibrium with chromium.

#### REFERENCES

- [55Par] E.Parthé,H.Nowotny and H.Schmidt,"Structural Investigation of Silicides",Monatsh.Chem. 86 (1955) 385-396
- [56Now] H.Nowotny,B.Lux and H.Kudielka,"The Behavior of Metal Rich, High Melting Silicides Versus Boron,Carbon,Nitrogen and Oxygen",Monath.Chem.87 (1956) 447-470
- [66Mue] K.Müller and H.Rebsch,"Silicon Nitride - Corrosion Resistant and Stable Against Aluminium",Silikattechnik 17 (1966) 279-282
- [69Fel] H.Feld,E.Gugel and H.G.Nitzsche,"Silicon Nitride - A Corrosion Resistant High Temperature Material",Werkstoffe Korros. 20 (1969) 571-574
- [71Sve] V.N.Svechnikov,G.F.Kobchenko,V.G.Vanchenko and E.L.Martynchuk,"The System Chromium - Nitrogen",Diagrammy Sost.Metall.Syst. (Nauka,Moskow,1971) 135
- [73Cha] J.A.Champion,B.J.Keene and S.Allen,"Wetting of Refractory Materials by Molten Metallides"J.Mater.Sci.8 (1973) 423-426
- [75Cha] T.Chart,"Thermodynamic Properties of the Tungsten - Silicon and Chromium - Silicon Systems",Met.Sci.9 (1975) 504-509
- [76Kri] Y.I.Krilov and V.A.Bronnikov,"Thermit Mixtures on the Basis of Exothermal Reactions of BN and  $\text{Si}_3\text{N}_4$  with Metals",Poroshk. Met.(1) (1976) 52-55
- [76Mof] W.Moffatt,"The Handbook of Binary Phase Diagrams", (General Electric Comp.,Schenectady,NY,1976 and updates)
- [76Fro] E.Fromm and E.Gebhardt,"Gase und Kohlenstoff in Metallen" (Springer,Berlin,1976)
- [77Kha] A.P.Khalepa,"Study of the Solid Phase Reactions of  $\text{Si}_3\text{N}_4$  with Cr,Mo and W",Issled.Obl.Novykh.Materialov (1977) 128-131

- [81Kat] T.Kato, M.Yoshimura and S.Somiya, "Reactions and Phase Relations in the System Cr-Si-N at 1600°C under 1 Atm N<sub>2</sub>", *Yogyo Kyokai Shi* 89 (1981) 221-229
- [81Yam] J.Yamaguchi, N.Kieda, K.Uematsu, N.Mizutani and M.Kato, "Phase Relations and Non-Stoichiometry of Cr-N-System", *Nippon Kagaku Kaishi* 10 (1981) 1529-1533
- [83Ore] T.W.Orent and R.A.Wagner, "Investigation of the Chemical Bonding of Cr and Ti to Silicon Nitride", *J.Vac.Sci.Technol.* B1 (1983) 844-849
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [88Sch] J.C.Schuster, "Silicon Nitride - Metal Joints: Phase Equilibria in the Systems Si<sub>3</sub>N<sub>4</sub> - Cr, Mo, W and Re", *J.Mater.Sci.* 23 (1988) 2792-2796
- [89Got] I.Gotman and E.Y.Gutmanas, "Interaction of Si<sub>3</sub>N<sub>4</sub> with Chromium Powder", *J.Mater.Sci.Lett.* 8 (1989) 1103-1106

Table 19.1: Solid phases in the system Cr - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Cr	cI2 Im $\bar{3}$ m W (A2)	a= 288.4	[85Vil]; powder pattern: ASTM file card # 6-694
Cr <sub>5</sub> Si	cP8 Pm $\bar{3}$ n Cr <sub>5</sub> Si (A15)	a= 455.5	[85Vil]; powder pattern: ASTM file card # 7-186
Cr <sub>5</sub> Si <sub>2</sub>	tI32 I4/mcm Si <sub>5</sub> W <sub>2</sub> (D8 <sub>m</sub> )	a= 917.0 c= 463.6	[85Vil]; powder pattern: given in [55Par]
CrSi	cP8 P2 <sub>1</sub> 3 FeSi (B20)	a= 460.7	[85Vil]; powder pattern:
CrSi <sub>2</sub>	hP9 P6 <sub>2</sub> 22 CrSi <sub>2</sub> (C40)	a= 443.1 c= 636.4	[85Vil]; powder pattern: ASTM file card # 12-596 35-781
Cr <sub>2</sub> N	hP9 P $\bar{3}$ 1m	a= 479.6 c= 447.0	[85Vil]; powder pattern: ASTM file card # 27-127 35-803
CrN	cF8 Fm $\bar{3}$ m NaCl (B1)	a= 414.8	[85Vil]; powder pattern: ASTM file card # 11-65
Si	cF8 Fd $\bar{3}$ m C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160

Tab.19.2: Thermodynamic data for the solid phases in Cr - Si - N

phase	$\Delta G_f^\circ$ (J/gramatom)	Comment
.1429 $\text{Si}_3\text{N}_4$	$-124602 + 57.95 \text{ T}$	[76Fro]
.3333 $\text{CrSi}_2$	$-26700 + 1.0 \text{ T}$	[75Cha]
.5000 $\text{CrSi}$	$-27400 - 0.6 \text{ T}$	[75Cha]
.1250 $\text{Cr}_3\text{Si}_3$	$-27500 - 0.8 \text{ T}$	[75Cha]
.2500 $\text{Cr}_5\text{Si}$	$-26400 + 0.6 \text{ T}$	[75Cha]
Cr(s.s.7at% Si)	-7200 (at 1673K)	estimated from plot $\Delta G_f^{1673}$ vs. $x_{\text{Si}}$
Cr(s.s.6at% Si)	-6700 (at 1273K)	estimated from plot $\Delta G_f^{1273}$ vs. $x_{\text{Si}}$
.3632 $\text{Cr}_2\text{N}_{0.75}$	$-30663.4 + 15.22 \text{ T}$	[76Fro]

Tab.19.3: Calculated invariant equilibria in Cr - Si - N

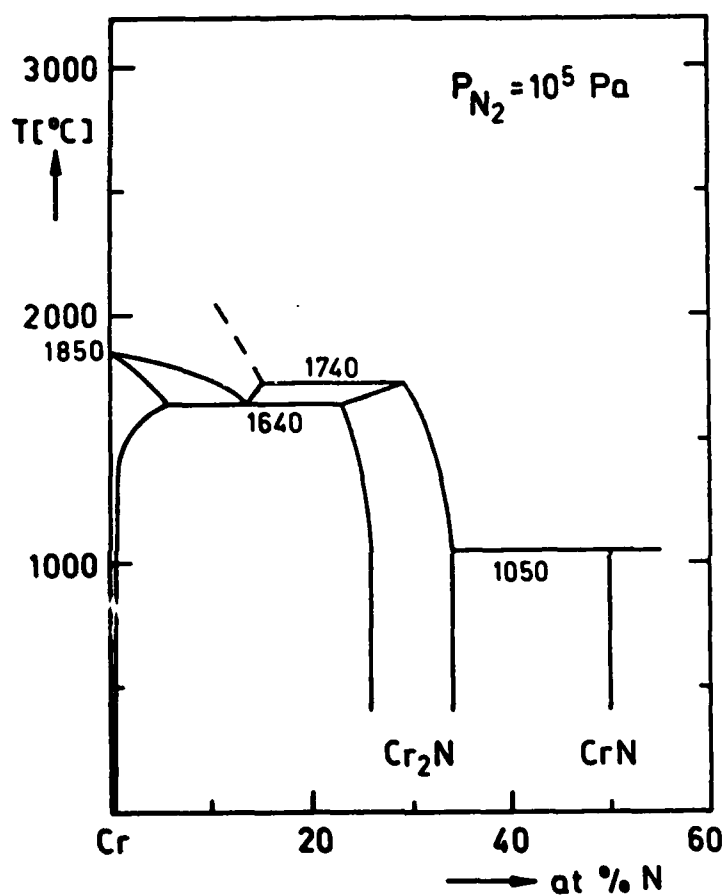
a) at 1000°C (1273K):

$p(N_2)$ (Pa)	Reaction
$5 \times 10^{-2}$	$Si_3N_4 = 3 Si + 2 N_2$
$85 \times 10^{-2}$	$Si_3N_4 + 6 Cr_{.5}Si_{.5} = 9 Cr_{.333}Si_{.667} + 2 N_2$
$220 \times 10^{-2}$	$Si_3N_4 + 12 Cr_{.625}Si_{.375} = 15 Cr_{.5}Si_{.5} + 2 N_2$
2.2	$Si_3N_4 + 15 Cr_{.75}Si_{.25} = 18 Cr_{.625}Si_{.375} + 2 N_2$
42	$Cr_2N_{.75} = 2 Cr + 0.38 N_2$
830	$Si_3N_4 + 4.5 Cr_2N_{.75} = 12 Cr_{.75}Si_{.25} + 3.71 N_2$

b) at 1400°C (1673K)

$p(N_2)$ (Pa)	Reaction
95	$Si_3N_4 = 3 Si + 2 N_2$
680	$Si_3N_4 + 6 Cr_{.5}Si_{.5} = 9 Cr_{.333}Si_{.667} + 2 N_2$
$1.7 \times 10^3$	$Si_3N_4 + 12 Cr_{.625}Si_{.375} = 15 Cr_{.5}Si_{.5} + 2 N_2$
$6.6 \times 10^3$	$Cr_2N_{.75} = 2 Cr + 0.38 N_2$
$13.8 \times 10^3$	$Si_3N_4 + 15 Cr_{.75}Si_{.25} = 18 Cr_{.625}Si_{.375} + 2 N_2$
$250 \times 10^3$	$Si_3N_4 + 4.5 Cr_2N_{.75} = 12 Cr_{.75}Si_{.25} + 3.71 N_2$

Fig.19.1: Phase diagram of the boundary system chromium - nitrogen



**Fig.19.2: Isothermal section observed in the system Cr - Si - N  
at 1000°C (in the absence of external nitrogen pressure)**

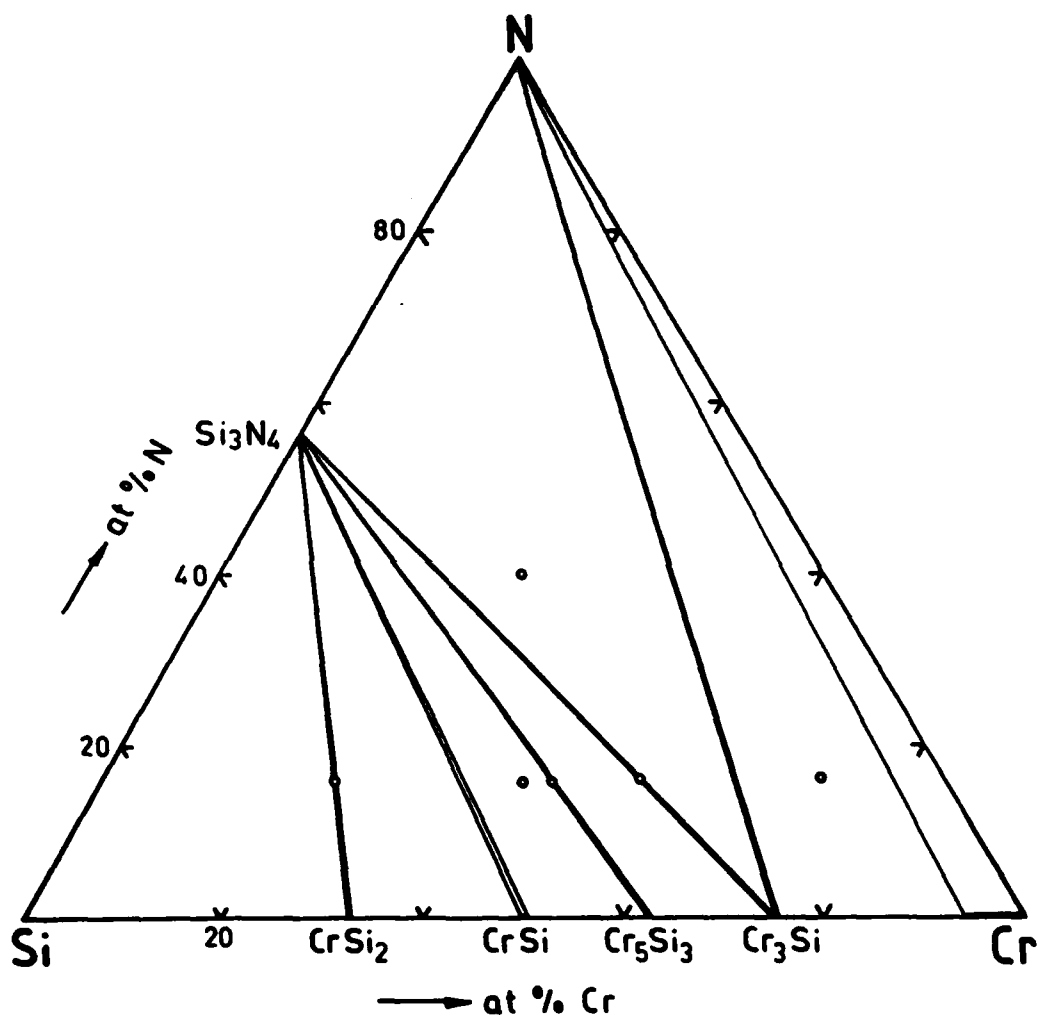
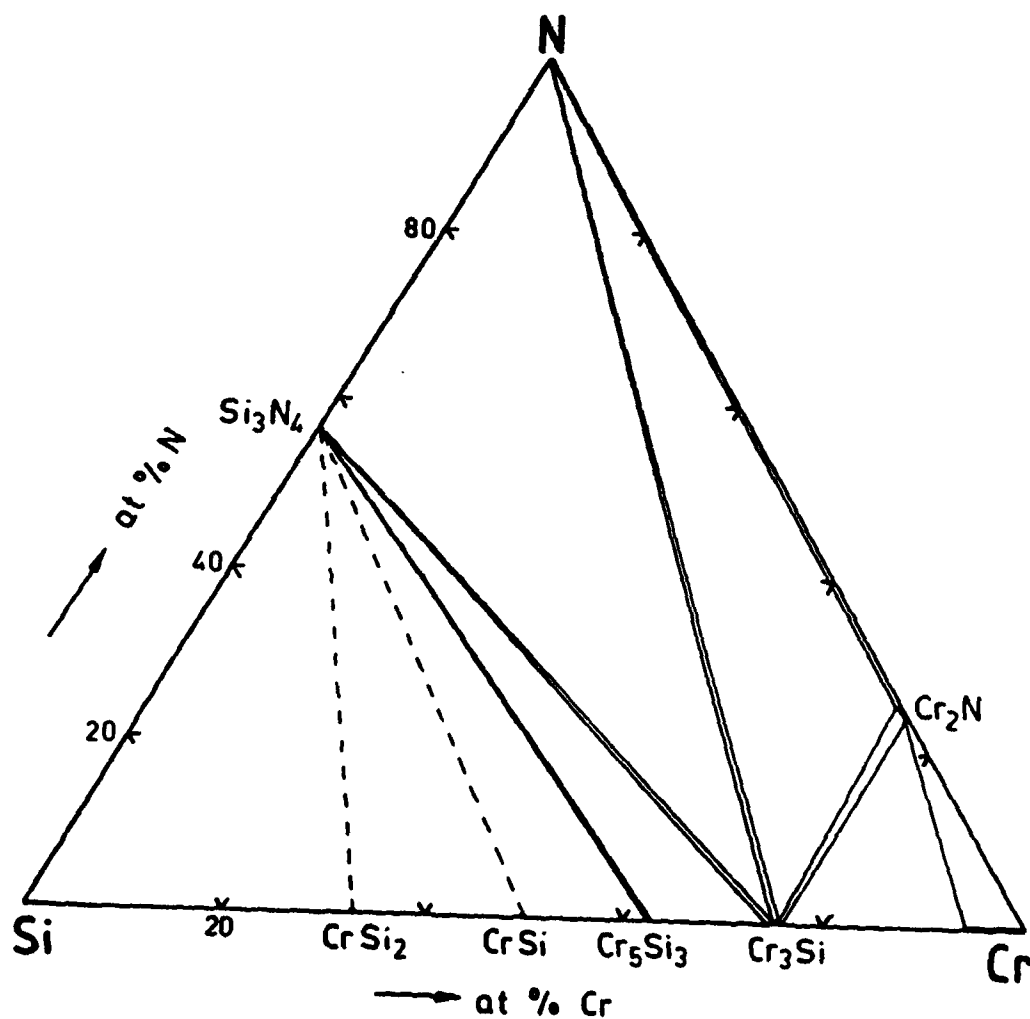




Fig.19.3: Isothermal section observed in the system Cr - Si - N  
at 1000°C (under a nitrogen partial pressure above  $\approx 40$  Pa)



**Fig.19.4: Isothermal section observed in the system Cr -Si - N  
at 1400°C (under argon)**

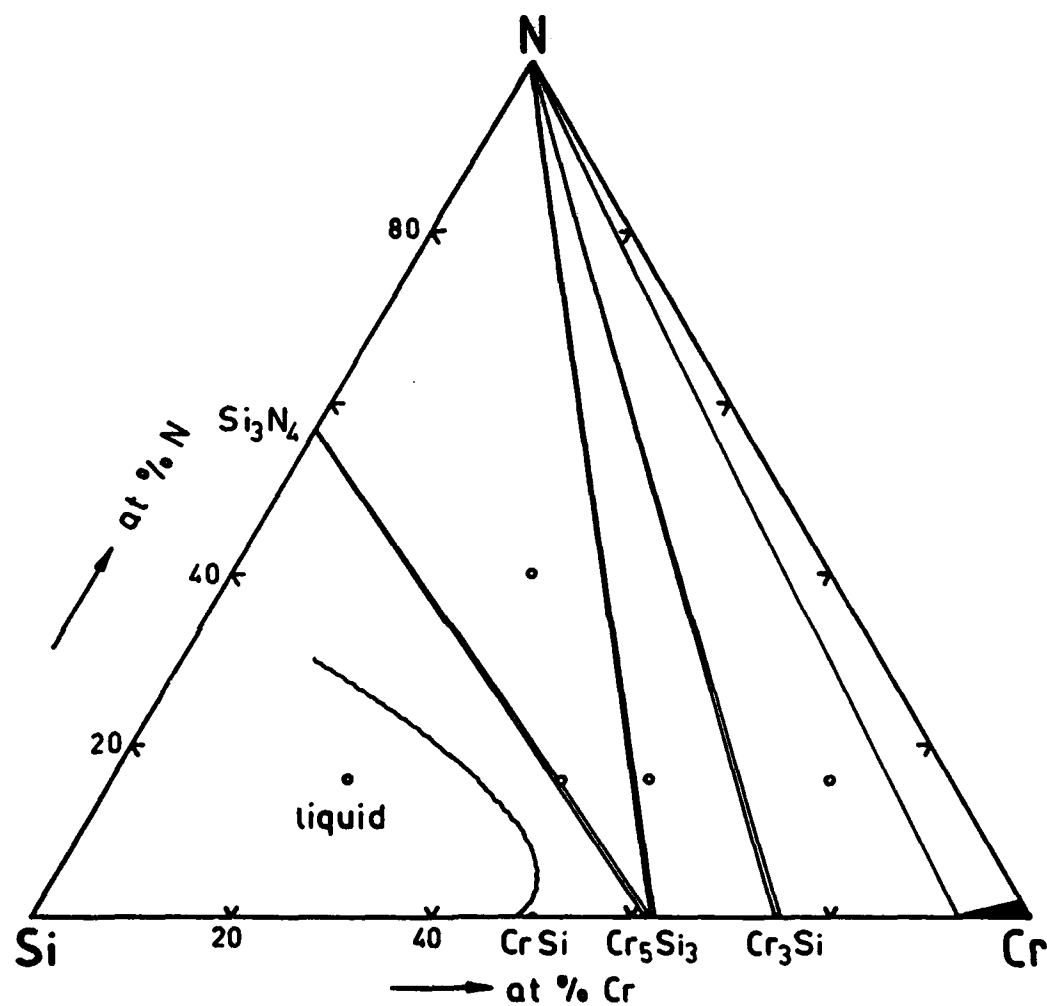
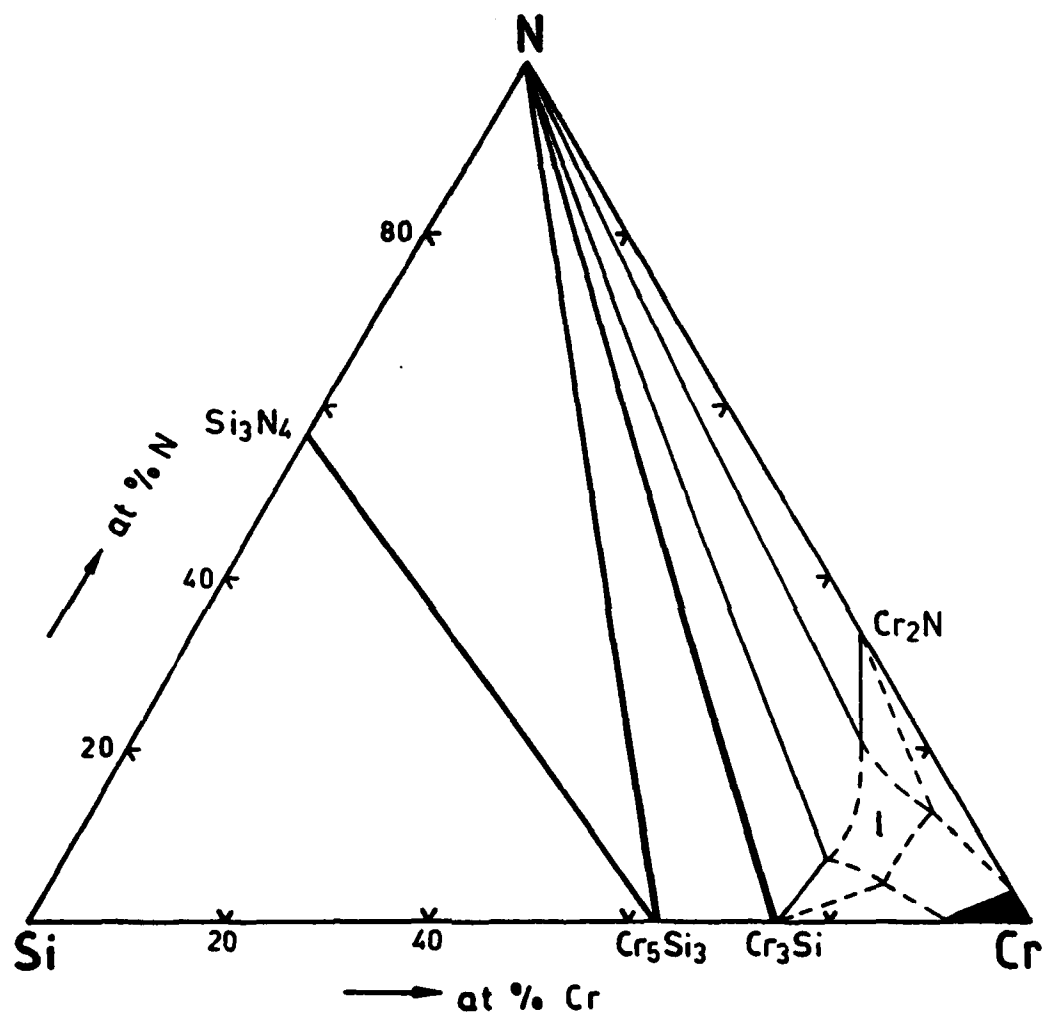


Fig.19.5: Isothermal section observed in the system Cr - Si - N  
at 1600°C (under  $p(N_2) = 10^5$  Pa)



## SYSTEM MOLYBDENUM - SILICON - NITROGEN (Mo-Si-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria of Mo-Si-N between 1000°C and 1400°C were determined by x-ray analysis [88Sch]. The alloys investigated were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si, from Alpha Div., Ventron Corp., USA), silicon (purity: 3N, from Alpha Div., Ventron Corp., USA) and molybdenum (purity: 3N, from Metallwerk Plansee, Austria). Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 400h at temperatures up to 1000°C or annealed in an r.f. furnace under argon (purity: 5N+) at temperatures up to 1400°C.

### BINARY SYSTEMS

The phase diagram for the binary system Mo-Si given in [86Mas] (based on [72Koc], thermodynamically modelled by [89Vah]) needs to be modified with regard to the melting behavior of  $\text{Mo}_5\text{Si}$  [54Now], [80Zot], [83Chr]:  $\text{Mo}_5\text{Si}$  decomposes upon melting into  $\text{Mo}_5\text{Si}_2 + (\text{liq.})$  rather than  $\text{Mo} + (\text{liq.})$  (fig.20.1). Three intermediate phases occur (tab.20.1). The phase diagram for the system Mo-N given in [86Mas] is based on [70Ett] and [78Jeh] but does not include the occurrence of  $\beta\text{-Mo}_3\text{N}$  at  $T \leq 850^\circ\text{C}$  as shown in the original diagrams (fig.20.2 due to [70Ett], [78Jeh], reviewed by [80Fer]). The intermediate phases are listed in tab.20.1. Neither is stable at 1000°C unless  $p(\text{N}_2) > 10^5 \text{ Pa}$  [78Jeh]. No phase diagram is reported for Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.20.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Mo-Si-N (tab.20.1). At 1000°C as well as at 1400°C  $\text{Si}_3\text{N}_4$  coexists with  $\text{MoSi}_2$  and  $\text{Mo}_5\text{Si}_2$  but not with  $\text{Mo}_5\text{Si}$  or Mo (fig.20.3). In the absence of external nitrogen pressure no

molybdenum nitride is observed [88Sch]. This confirms earlier reports on the decomposition of  $\text{Si}_3\text{N}_4$  in contact with molybdenum at temperatures of 1000°C and above [56Now], [69Fit], [77Kha], [79Mue], [83Sug]. However at temperatures up to 1000°C this reaction is slow and incomplete even after 400h anneal [88Sch]. Lattice parameters of neither molybdenum silicide coexisting with  $\text{Si}_3\text{N}_4$  or  $\text{N}_2$  gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in molybdenum silicides.

Using the thermodynamic data in tab.20.2 the nitrogen pressures for the invariant equilibria occurring at 1000°C as well as at 1400°C are calculated (tab.20.3). The resulting tie lines are consistent with the experimentally observed isothermal section (fig.20.3).

#### REFERENCES

- [54Now] H.Nowotny, E.Parthé, R.Kieffer and F.Benesovsky, "The Ternary Molybdenum - Silicon - Carbon", *Monatsh.Chem.* 85 (1954) 255-272
- [56Now] H.Nowotny, B.Lux and H.Kudielka, "The Behavior of Metal Rich, High Melting Silicides Versus Boron, Carbon, Nitrogen and Oxygen", *Monatsh.Chem.* 87 (1956) 447-470
- [69Fit] E.Fitzer and K.Reinmuth, "The Reaction of High Melting Silicides with Nitrogen and Oxygen", *Proc.6th.Int.Plansee Sem.* (Reutte, Austria, 1969) 767-802
- [70Ett] P.Ettmayer, "The System Molybdenum - Nitrogen", *Monatsh.Chem.* 101 (1970) 127-140
- [72Koc] Y.A.Kocherzhinsky, "Differential Thermal Analysis at High Temperatures", *Colloqu.Int.CNRS No.205* (1972) 50-51
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [77Kha] A.P.Khalepa, "Study of the Solid Phase Reactions of  $\text{Si}_3\text{N}_4$  with Cr, Mo and W", *Issled.Obl.Novykh.Materialov* (1977) 128-131
- [78Jeh] H.Jehn and P.Ettmayer, "The Molybdenum - Nitrogen Phase Diagram", *J.Less Common Met.* 58 (1978) 85-98
- [79Mue] A.Müller-Zell and H.W.Hennicke, "Joining Techniques for Silicon Nitride and Silicon Carbide Mixed or in Contact with High Melting Metals", *BMFT Report T 79-124* (Fachinformationszentrum Eggenstein-Leopoldshafen, FRG, 1979)
- [80Fer] R.Ferro and R.Marazza, "The Mo-N (Molybdenum - Nitrogen) System", *Bull.Alloy Phase Diagr.* 1 (1980) 82-85
- [80Zot] Y.P.Zotov, N.N.Kroshkina and V.E.Bukharin, "Determination of the Composition and Melting Points of Eutectics in Refractory Metal (Alloy) - Silicon Systems", *Izv.Akad.Nauk SSSR, Neorg.Mater.* 16 (1980) 842-845

- [83Chr] A.N.Christensen, "Preparation and Characterisation of  $\text{Mg Si}$  and  $\text{Mg}_2\text{Si}$ ", *Acta Chem.Scand.* A37 (1983) 519-522
- [83Sug] K.Suganuma, T.Okamoto, M.Shimada and M.Koizumi, "New Method for Solid State Bonding Between Ceramics and Metals", *J.Amer.Ceram. Soc.* 66 (1983) C117-C118
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [88Sch] J.C.Schuster, "Silicon Nitride - Metal Joints: Phase Equilibria in the Systems  $\text{Si}_3\text{N}_4$  - Cr, Mo, W and Re", *J.Mater.Sci.* 23 (1988) 2792-2796
- [89Vah] C.Vahlas, P.Y.Chevalier and E.Blanquet, "A Thermodynamic Evaluation of Four Si-M (M= Mo, Ta, Ti, W) Binary Systems", *CALPHAD* 13 (1989) 273-292

Table 20.1: Solid phases in the system Mo - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Mo	CI2 Im $\bar{3}$ m W (A2)	a= 314.70	[85Vil]; powder pattern: ASTM file card # 4-809
Mo <sub>3</sub> Si	CP8 Pm $\bar{3}$ n Cr <sub>3</sub> Si (A15)	a= 489.0	[85Vil]; powder pattern: ASTM file card # 4-814
Mo <sub>3</sub> Si <sub>3</sub>	tI32 I4/mcm Si <sub>3</sub> W <sub>3</sub> (D8 <sub>m</sub> )	a= 964.25 c= 490.96	[85Vil]; powder pattern: ASTM file card # 17-415
MoSi <sub>2</sub>	tI6 I4/mmm MoSi <sub>2</sub> (C11)	a= 320.2 c= 785.1	[85Vil]; powder pattern: ASTM file card # 6-681
$\beta$ Mo <sub>2</sub> N T<850	tI12 I4 <sub>1</sub> /amd Mo <sub>2</sub> N	a= 420 c= 801	[85Vil]; powder pattern: ASTM file card # 24-768
$\gamma$ Mo <sub>2</sub> N (or Mo <sub>3</sub> N <sub>2</sub> ) T>850	CP8 Pm $\bar{3}$ m	a= 416.5	[85Vil]; powder pattern: ASTM file card # 25-1366
$\delta$ MoN	hP16 P6 <sub>3</sub> /mmc MoN	a= 572.5 c= 560.8	[85Vil]; powder pattern: ASTM file card # 25-1367
Si	CF8 Fd $\bar{3}$ m C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160

Tab.20.2: Thermodynamic data for the solid phases in Mo - Si - N

phase	$\Delta G_f^\circ$ [J/gramatom]	Comment
.1429 $\text{Si}_3\text{N}_4$	$-124602 + 57.95 T$	[76Fro]
.3333 $\text{MoSi}_2$	$-46515.7 - 2.832 T$	[89Vah]
.1250 $\text{Mo}_2\text{Si}_3$	$-37008 - 3.787 T$	[89Vah]
.2500 $\text{Mo}_2\text{Si}$	$-29710 + 0.510 T$	[89Vah]
.3333 $\text{Mo}_2\text{N}$	$-19107.4 + 17.96 T$	[76Fro]

Tab.20.3: Calculated invariant equilibria in Mo - Si - N

a) at 1000°C (1273K):

$P(\text{N}_2)$ (Pa)	Reaction
$5 \times 10^{-3}$	$\text{Si}_3\text{N}_4 = 3 \text{ Si} + 2 \text{ N}_2$
23.6	$\text{Si}_3\text{N}_4 + 3.429 \text{ Mo}_{.025}\text{Si}_{.375} = 6.429 \text{ Mo}_{.333}\text{Si}_{.667} + 2 \text{ N}_2$
$6.4 \times 10^3$	$\text{Si}_3\text{N}_4 + 15 \text{ Mo}_{.75}\text{Si}_{.25} = 18 \text{ Mo}_{.025}\text{Si}_{.375} + 2 \text{ N}_2$
$12 \times 10^3$	$\text{Mo}_2\text{N} = 2 \text{ Mo} + 0.5 \text{ N}_2$
$39.5 \times 10^3$	$\text{Si}_3\text{N}_4 + 4.5 \text{ Mo}_2\text{N} = 12 \text{ Mo}_{.75}\text{Si}_{.25} + 4.24 \text{ N}_2$

b) at 1400°C (1673K)

$P(\text{N}_2)$ (Pa)	Reaction
95	$\text{Si}_3\text{N}_4 = 3 \text{ Si} + 2 \text{ N}_2$
$64 \times 10^3$	$\text{Si}_3\text{N}_4 + 3.429 \text{ Mo}_{.025}\text{Si}_{.375} = 6.429 \text{ Mo}_{.333}\text{Si}_{.667} + 2 \text{ N}_2$
$10 \times 10^6$	$\text{Si}_3\text{N}_4 + 15 \text{ Mo}_{.75}\text{Si}_{.25} = 18 \text{ Mo}_{.025}\text{Si}_{.375} + 2 \text{ N}_2$
$11 \times 10^6$	$\text{Mo}_2\text{N} = 2 \text{ Mo} + 0.5 \text{ N}_2$
$22 \times 10^6$	$\text{Si}_3\text{N}_4 + 4.5 \text{ Mo}_2\text{N} = 12 \text{ Mo}_{.75}\text{Si}_{.25} + 4.24 \text{ N}_2$



Fig.20.1: Phase diagram of the boundary system molybdenum - silicon

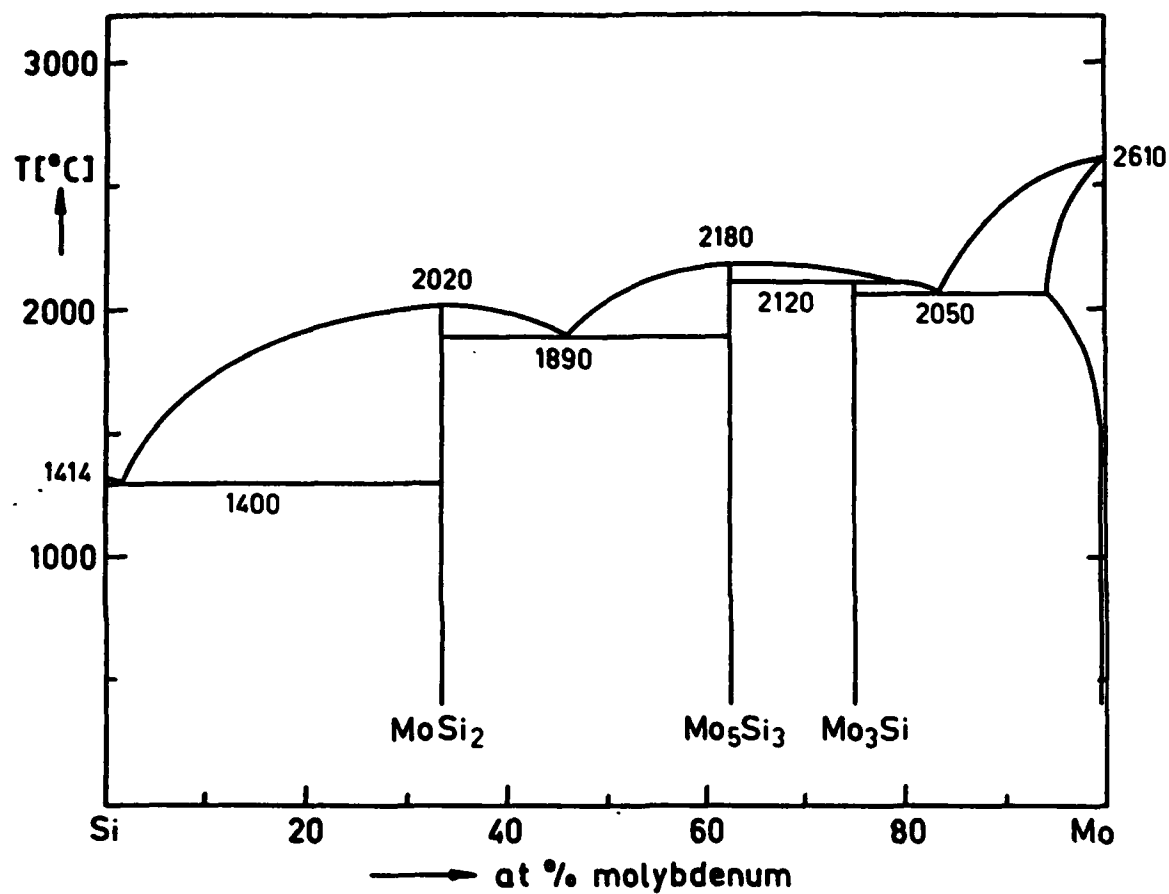


Fig.20.2: Phase diagram of the boundary system molybdenum - nitrogen

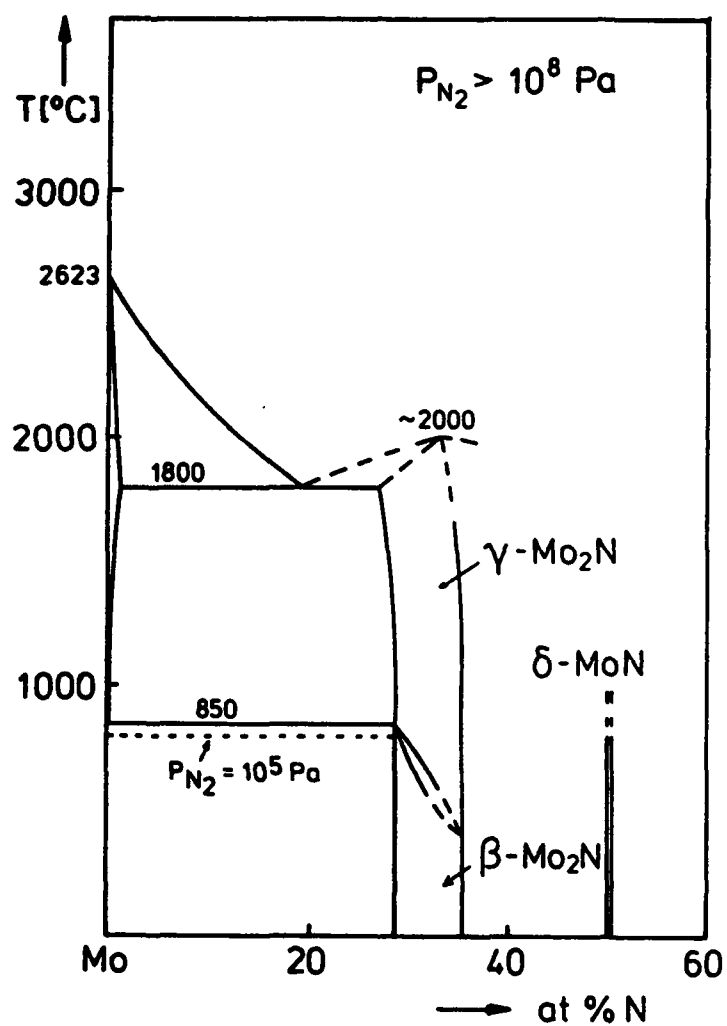
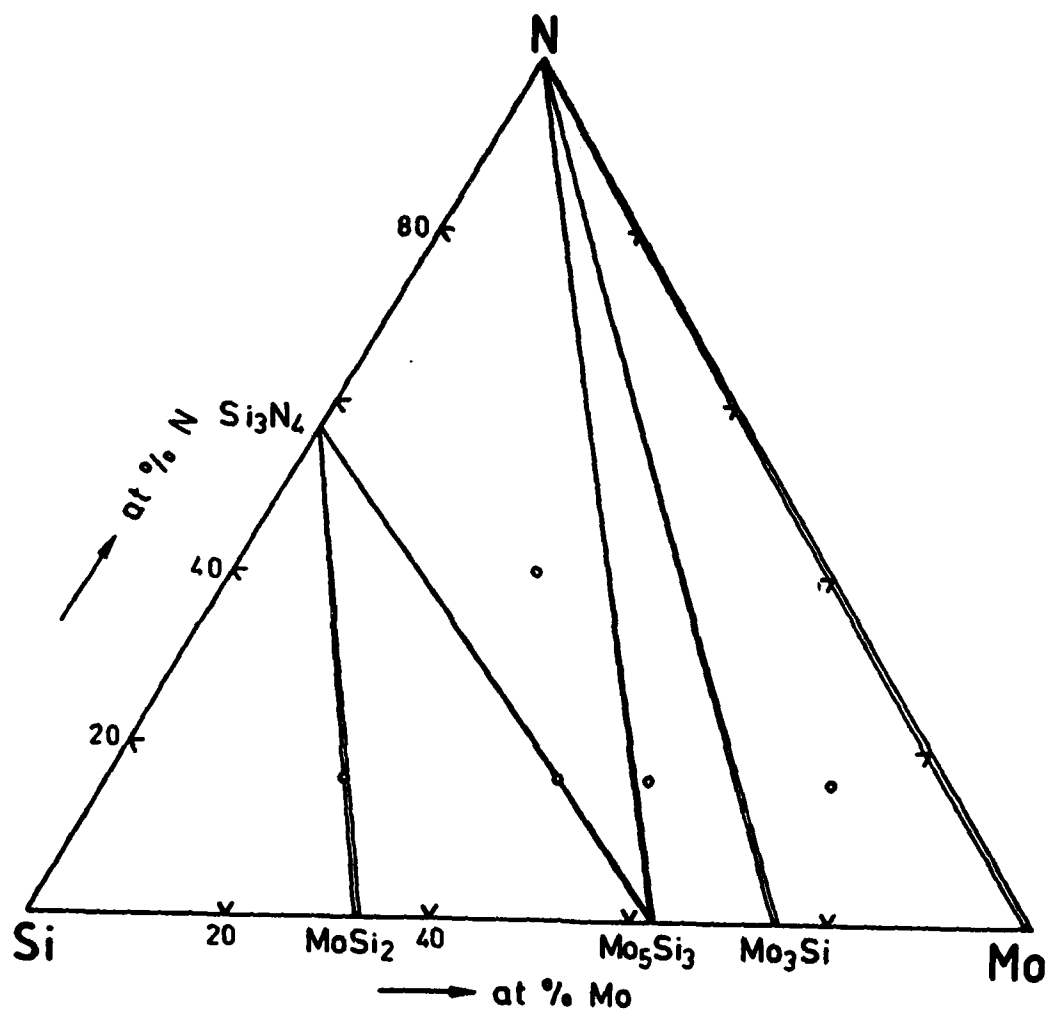


Fig.20.3: Isothermal section observed in the system Mo - Si - N  
at 1400°C under argon (At 1000°C identical tie lines exist)



## SYSTEM TUNGSTEN - SILICON - NITROGEN (W-Si-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria of W-Si-N between 1000°C and 1400°C were determined by x-ray analysis [88Sch]. The alloys investigated were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si, from Alpha Div., Ventron Corp., USA), silicon (purity: 3N, from Alpha Div., Ventron Corp., USA) and tungsten (purity: 3N, from Metallwerk Plansee, Austria). Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 400h at temperatures up to 1000°C or annealed in an r.f. furnace under argon (purity: 5N+) at temperatures up to 1400°C.

### BINARY SYSTEMS

The phase diagram for the binary system W-Si is given in [86Mas] and was thermodynamically modelled by [89Vah]. No phase diagram exist for the systems W-N or Si-N. Two supposedly stable [88Wri] tungsten nitrides are reported (tab. 21.1). However, the cubic phase ( $\beta$ )- $\text{W}_2\text{N}$  was shown to be an oxynitride [67Gue].  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab. 21.1). The solubility of nitrogen in silicon as well as tungsten is very low [76Fro], [81Jeh].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in W-Si-N (tab. 21.1). Figs. 21.1 and 21.2 show the phase equilibria in the absence of external nitrogen pressure at 1000°C and 1400°C resp. [88Sch].  $\text{Si}_3\text{N}_4$  coexists with tungsten up to 1128°C [88Sch]. Above this temperature  $\text{Si}_3\text{N}_4$  is rapidly decomposed [69Fit], [70Sat], [77Kah], [79Mue], [88Sch] and a three phase field  $\text{Si}_3\text{N}_4 + \text{W}_2\text{Si}_5 + \text{N}_2(\text{gas})$  exists. Lattice parameters of neither tungsten silicide coexisting with  $\text{Si}_3\text{N}_4$  or  $\text{N}_2$  gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in tungsten silicides.

Using the thermodynamic data in tab.21.2 the nitrogen pressures for the invariant equilibria occurring at 1000°C as well as at 1400°C are calculated (tab.21.3). The resulting tie lines are consistent with the experimentally observed isothermal sections (figs.21.1 and 21.2). For the observed onset of the decomposition reaction of  $\text{Si}_3\text{N}_4$  with tungsten at 1128°C the calculated nitrogen equilibrium pressure is 376 Pa.

#### REFERENCES

- [67Gue] F.Günther and H.G.Schneider, "Structure of Cubic Tungsten Nitride", *Sov.Phys.-Crystallogr.* 11 (1967) 585-587
- [69Fit] E.Fitzer and K.Reinmuth, "The Reaction of High Melting Silicides with Nitrogen and Oxygen", *Proc.6th.Int.Plansee Sem.* (Reutte, Austria, 1969) 767-802
- [70Sat] T.Sato and T.Urano, "Reactions Between Refractory Metals and Insulating Nitrides at High Temperatures", *Yogyo Kyokai Shi* 78 (1970) 21-29
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [77Kha] A.P.Khalepa, "Study of the Solid Phase Reactions of  $\text{Si}_3\text{N}_4$  with Cr, Mo and W", *Issled.Obl.Novykh.Materialov* (1977) 128-131
- [79Mue] A.Müller-Zell and H.W.Hennicke, "Joining Techniques for Silicon Nitride and Silicon Carbide Mixed or in Contact with High Melting Metals", *BMFT Report T 79-124* (Fachinformationszentrum Eggenstein-Leopoldshafen, FRG, 1979)
- [81Jeh] H.Jehn and P.Ettmayer, "High Pressure Investigations of the Solubility of Nitrogen in Tungsten", *Monatsh.Chem.* 111 (1981) 1437-1440
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [88Sch] J.C.Schuster, "Silicon Nitride - Metal Joints: Phase Equilibria in the Systems  $\text{Si}_3\text{N}_4$  - Cr, Mo, W and Re", *J.Mater.Sci.* 23 (1988) 2792-2796
- [89Vah] C.Vahlas, P.Y.Chevalier and E.Blanquet, "A Thermodynamic Evaluation of Four Si-M (M= Mo, Ta, Ti, W) Binary Systems", *CALPHAD* 13 (1989) 273-292
- [89Wri] H.A.Wriedt, "The N - W (Nitrogen - Tungsten) System", *Bull. Alloy Ph.Diagr.* 10 (1989) 358-367

Table 21.1: Solid phases in the system W - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
W	cI2 Im $\bar{3}m$ W (A2)	a= 316.52	[85V11]; powder pattern: ASTM file card # 4-806
W <sub>5</sub> Si <sub>3</sub>	tI32 I4/mcm W <sub>5</sub> Si <sub>3</sub> (D8 <sub>m</sub> )	a= 964.5 c= 497.0	[85V11]; powder pattern: ASTM file card # 16-261
WSi <sub>2</sub>	tI6 I4/mmm MoSi <sub>2</sub> (C11)	a= 321.1 c= 786.8	[85V11]; powder pattern: ASTM file card # 11-195
$\beta$ -W <sub>2</sub> N (W <sub>3</sub> N <sub>4</sub> )	cF8 Fm $\bar{3}m$ NaCl (B1)	a= 412.6	[85V11]; powder pattern: ASTM file card # 25-1257
$\delta$ -WN	hP2 P6 $\bar{3}$ m2 WC (B <sub>1</sub> )	a= 289.3 c= 282.6	[85V11]; powder pattern: ASTM file card # 35-1256
Si	cF8 Fd $\bar{3}m$ C (A4)	a= 542.86	[85V11]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85V11]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85V11]; powder pattern: ASTM file card # 29-1132 33-1160

Tab.21.2: Thermodynamic data for the solid phases in W - Si - N

phase	$\Delta G_f^\circ$ [J/gramatom]	Comment
.1429 $\text{Si}_3\text{N}_4$	-124602 + 57.95 T	[76Fro]
.3333 $\text{WSi}_2$	-31039 + 0.697 T	[89Vah]
.1250 $\text{W}_5\text{Si}_3$	-19203.8 - 1.778 T	[89Vah]

Tab.21.3: Calculated invariant equilibria in W - Si - N

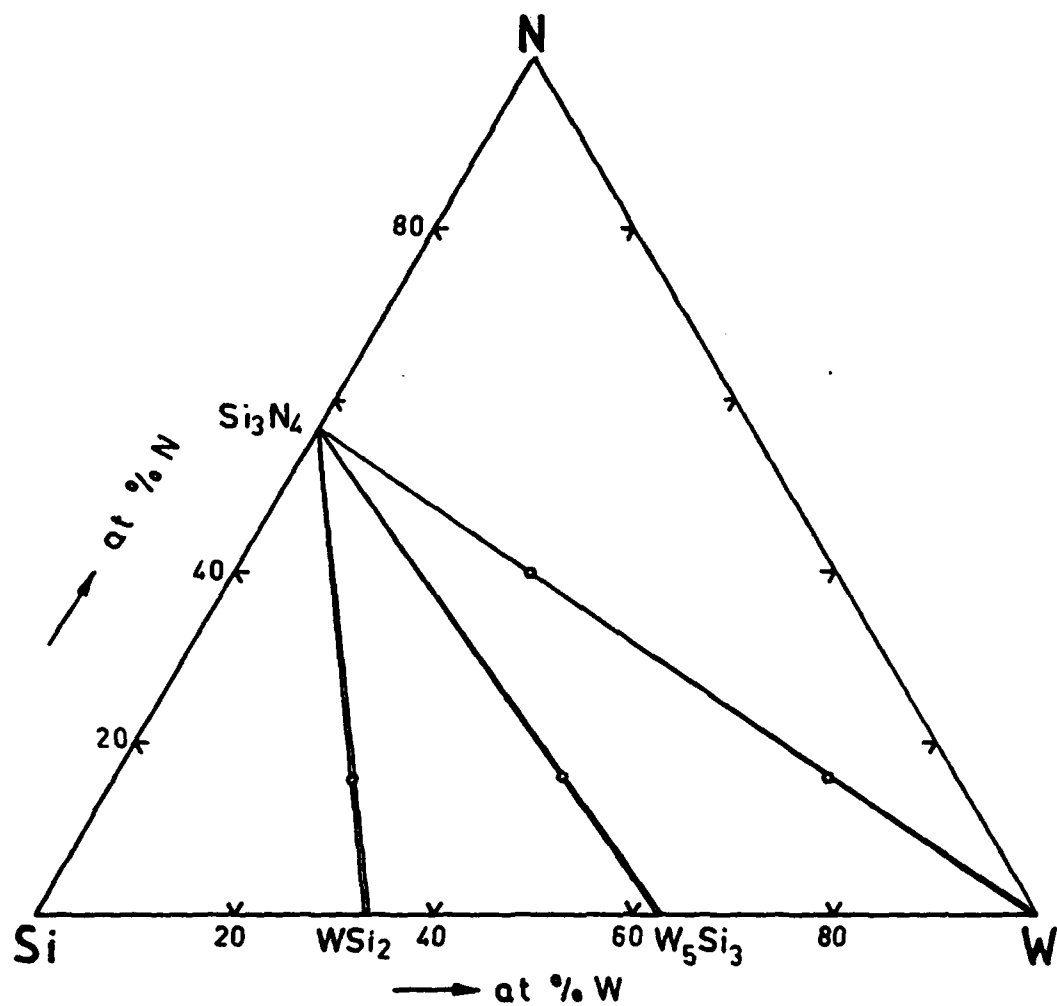
a) at 1000°C (1273K):

$p(\text{N}_2)$ (Pa)	Reaction
$5 \times 10^{-3}$	$\text{Si}_3\text{N}_4 = 3 \text{ Si} + 2 \text{ N}_2$
1.5	$\text{Si}_3\text{N}_4 + 3.429 \text{ W}_{.025} \text{Si}_{.375} = 6.429 \text{ W}_{.333} \text{Si}_{.667} + 2 \text{ N}_2$
17	$\text{Si}_3\text{N}_4 + 5 \text{ W} = 8 \text{ W}_{.025} \text{Si}_{.375} + 2 \text{ N}_2$

b) at 1400°C (1673K)

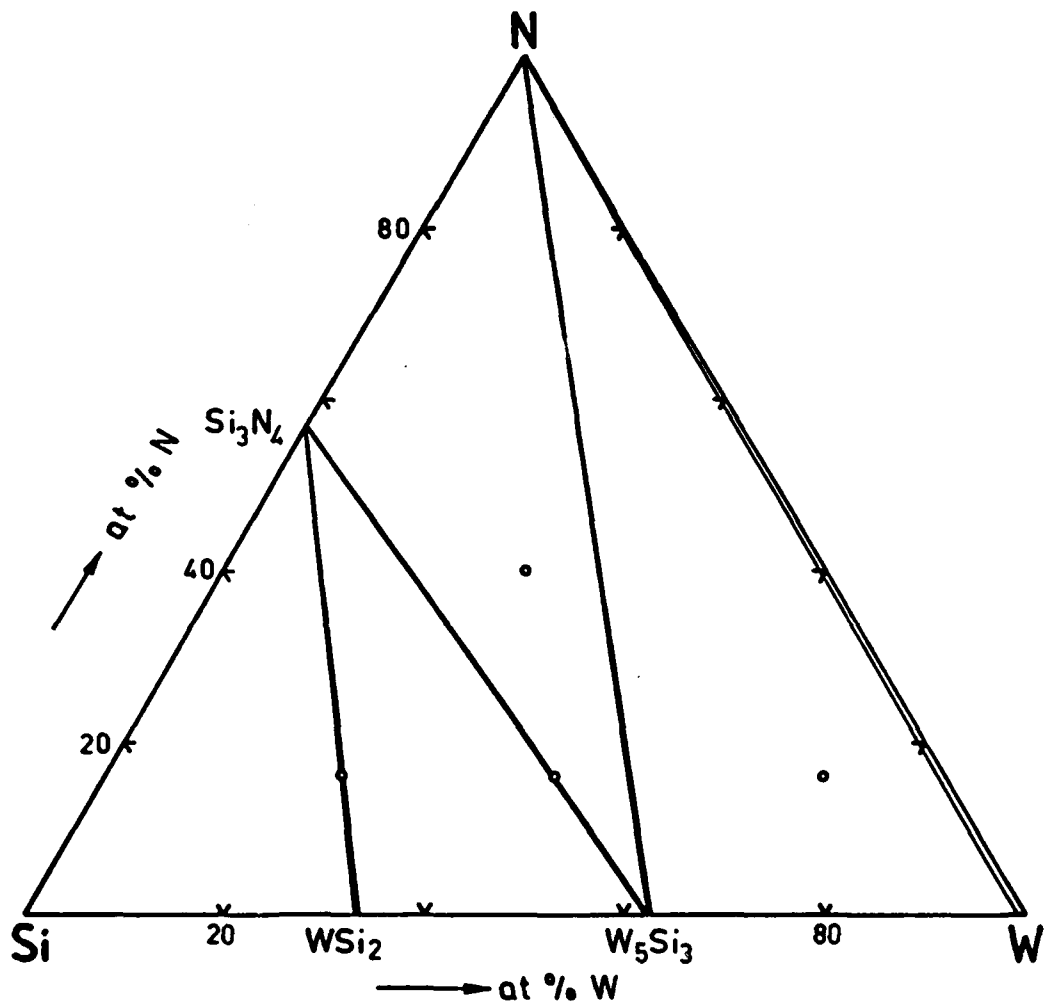
$p(\text{N}_2)$ (Pa)	Reaction
95	$\text{Si}_3\text{N}_4 = 3 \text{ Si} + 2 \text{ N}_2$
$6.22 \times 10^3$	$\text{Si}_3\text{N}_4 + 3.429 \text{ W}_{.025} \text{Si}_{.375} = 6.429 \text{ W}_{.333} \text{Si}_{.667} + 2 \text{ N}_2$
$56.6 \times 10^3$	$\text{Si}_3\text{N}_4 + 5 \text{ W} = 8 \text{ W}_{.025} \text{Si}_{.375} + 2 \text{ N}_2$

**Fig.21.1: Isothermal section observed in the system W - Si - N  
at 1000°C (in the absence of external nitrogen pressure)**





**Fig.21.2: Isothermal section observed in the system W - Si - N  
at 1400°C (under argon)**



## SYSTEM MANGANESE - SILICON - NITROGEN (Mn-Si-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria of the system Mn-Si-N were investigated at 1000°C by x-ray analysis [87Wei]. Alloys were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha$ - $\text{Si}_3\text{N}_4$  and  $\beta$ - $\text{Si}_3\text{N}_4$ , 58 at% Si), silicon (purity: 3N),  $\text{Mn}_2\text{N}$  (purity: 3N) from Alpha Div., Ventron Corp., USA and manganese (purity: 2N5) from Fluka AG., Switzerland. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were sealed in evacuated quartz tubes lined with Mo foil and heat treated at 1000°C.

### BINARY SYSTEMS

The phase diagram for the system Mn-Si is given in [86Mas] and was thermodynamically optimized by [89Cha]. The diagram for the system Mn-N given in [86Mas] was recently revised (fig.22.1 [90Gok]). Structural data for manganese silicides as well as the solid phases reported to form under nitrogen are listed in tab.22.1. No phase diagram is reported for Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha$ - $\text{Si}_3\text{N}_4$  and  $\beta$ - $\text{Si}_3\text{N}_4$  (tab.22.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

The ternary phase  $\text{MnSiN}_2$ , discovered by [71Mar], (tab.22.1) forms above 700°C by reaction of manganese with silicon under nitrogen [79Pom]. This phase is stable up to 1300°C under  $p(\text{N}_2) = 10^5 \text{ Pa}$  [79Pom]. The isothermal section at 1000°C [87Wei] (fig.22.2) shows  $\text{MnSiN}_2$  to coexist with  $\text{N}_2$  (gas),  $\text{Si}_3\text{N}_4$ ,  $\text{Mn}_2\text{Si}$ ,  $\beta$ -Mn(s.s.Si) and  $\gamma$ -Mn(s.s.N) under their equilibrium nitrogen partial pressure. Under argon  $\text{MnSiN}_2$  decomposes already above 800°C [79Pom]. Lattice parameters of  $\text{MnSiN}_2$  do not vary significantly with variation of the ratio Mn/Si in the alloys. Thus at 1000°C  $\text{MnSiN}_2$  is a line compound. The three phase field  $\text{MnSiN}_2 + \text{Mn}_2\text{Si} + \beta$ -Mn(s.s.Si) observed requires,

that phase fields with  $Mn_3Si_2$  participating must be cut off by a tie line between  $Mn_3Si$  and  $\beta\text{-Mn(s.s.Si)}$  at low nitrogen contents. Lattice parameters of neither manganese silicide coexisting with  $Si_3N_4$  or  $MnSiN_2$  are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in manganese silicides. Thus  $\beta\text{-Mn(s.s.Si)}$  is likely to dissolve  $N_2$ .

Using the thermodynamic data in tab.22.2 the nitrogen pressures for the invariant equilibria occurring at 1000°C are calculated (tab.22.3). The resulting tie lines are consistent with the experimentally observed isothermal section (fig.22.2).

#### REFERENCES

- [71Mar] R. Marchand, M. Maunaye and J. Lang, "On the Preparation of a Double Nitride of Silicon and Manganese", *Compt. Rend. Acad. Sci. Paris* C272 (1971) 1654-1656
- [75Gme] "Gmelins Handbook of Inorganic Chemistry, Manganese, Part C3", 8th ed. (Springer, Berlin, FRG, 1975) p231-251
- [75Kud] H. Kudielka and J. Grabke, "Investigation of the Phase Diagram Mn-N by X-Ray Diffraction at High Temperatures", *Z. Metallk.* 66 (1975) 469-471
- [76Fro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [79Pom] R. Pompe, "On the Solid State Reactions in the System Mn-Si-N", *Thermochim. Acta* 34 (1979) 245-256
- [84Jac] H. Jacobs and C. Stüve, "High Pressure Synthesis of the  $\eta$ -Phase in the System Mn-N:  $Mn_3N_2$ ", *J. Less Common Met.* 96 (1984) 323-329
- [85Vil] P. Villars and L.D. Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, OH., 1985)
- [86Mas] T.B. Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer. Soc. Met., Metals Park, OH., 1986)
- [87Wei] F. Weitzer and J.C. Schuster, "Phase Diagrams of the Ternary Systems Mn, Fe, Co, Ni-Si-N", *J. Solid State Chem.* 70 (1987) 178-184
- [89Cha] N. Chakraborti and H.L. Lukas, "Calculation and Optimization of The Mn-Si Phase Diagram", *CALPHAD* 13 (1989) 293-300
- [90Gok] N.A. Gokcen, "The Mn-N (Manganese-Nitrogen) System", *Bull. Alloy Phase Diagr.* 11 (1990) 33-42

Table 22.1: Solid phases at 1000°C in the system Mn - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\alpha$ -Mn(r) T<727	cI58 I $\bar{4}$ 3m $\alpha$ -Mn (A12)	a= 891.39	[85Vil];powder pattern: ASTM file card # 32-637
$\beta$ -Mn(h) 727<T<1100	cP20 P4 <sub>1</sub> 32 $\beta$ -Mn (A13)	a= 631.5	[85Vil],powder pattern: ASTM file card # 33-887
$\beta$ -Mn (s.s.15at% Si)		a= 628.3	[85Vil]
$\gamma$ -Mn(h) T>1100	cF4 Fm $\bar{3}$ m Cu (A1)	a= 386.2	[85Vil];powder pattern: ASTM file card # 1-1202 tetrag.dist.upon quench: ASTM file card # 17-910
$\gamma$ -Mn (s.s.10at% N)		a= 388	[75Kud]
Mn <sub>4</sub> Si <sub>9</sub> (Mn <sub>2</sub> Si, <sub>c</sub> MnSi) R $\bar{3}$ T<879	hR159	a= 1087.1 c= 1918.9	[85Vil];powder pattern: ASTM file card # 31-832 18-811,18-812
Mn <sub>2</sub> Si <sub>2</sub> ( <sub>c</sub> MnSi)	oI186 Immm	a= 1699.2 b= 2863.4 c= 465.6	labeled Mn <sub>4</sub> Si in [85Vil]; powder pattern: ASTM file card # 24-737
Mn <sub>3</sub> Si	cF16 Fm $\bar{3}$ m B1F <sub>2</sub> (DQ <sub>2</sub> )	a= 572.2	[85Vil];powder pattern:
Mn <sub>3</sub> Si <sub>2</sub> T<850	tP56 P4 <sub>1</sub> 2 <sub>1</sub> 2 Mn <sub>3</sub> Si <sub>2</sub>	a= 890.97 c= 871.53	[85Vil],powder pattern: ASTM file card # 29-896 30-826
Mn <sub>3</sub> Si <sub>3</sub>	hP16 P6 <sub>3</sub> /mcm Mn <sub>3</sub> Si <sub>3</sub> (DQ <sub>3</sub> )	a= 691.1 c= 481.3	[85Vil];powder pattern: ASTM file card # 3-1039
MnSi	cP8 P2 <sub>1</sub> 3 FeSi (B20)	a= 455.7	[85Vil]

cont.

Tab.22.1 continued:

$\text{MnSi}_{2-x}$  phases:

$\text{Mn}_{1.8}\text{Si}_{1.0}$ ( $\text{MnSi}_{1.720}$ )	tP120 $\text{P}\bar{4}\text{n}2$	a= 551.8 c= 4813.6	[85Vil]
$\text{Mn}_{2.0}\text{Si}_{1.5}$ ( $\text{MnSi}_{1.750}$ )	t**	a= 551.5 c= 1133.6	[85Vil]
$\text{Mn}_{1.5}\text{Si}_{2.0}$ ( $\text{MnSi}_{1.750}$ )	tI164 $\text{I}\bar{4}2\text{d}$	a= 553.1 c= 6531.1	[85Vil]; powder pattern: ASTM file card # 20-724
$\text{Mn}_{2.7}\text{Si}_{1.7}$ ( $\text{MnSi}_{1.741}$ )	tP296 $\text{P}\bar{4}\text{n}2$	a= 553 c= 1179.4	[85Vil]; powder pattern: ASTM file card # 26-1251
$\text{Mn}_4\text{Si}_7$ ( $\text{MnSi}_{1.75}$ )	tP44 $\text{P}\bar{4}\text{c}2$	a= 552.5 c= 1746.3	[85Vil]
c - $\text{Mn}_3\text{N}$	CP5 Fm3m $\text{Fe}_3\text{N}$ (L'1)	a= 394.2	[75Kud]
f - $\text{Mn}_2\text{N}$ phases :			
$\text{Mn}_2\text{N}_{1-x}$ (h) ( $0 < x < 0.33$ ) at $\approx 400^\circ\text{C}$	hP3 $\text{P}6_3/\text{mmc}$ $\text{Fe}_3\text{N}$ (L'3)	a= 281.60 c= 453.44	[85Vil]
$\text{Mn}_2\text{N}_{0.60}$ (r) ( $\text{Mn}_{1.2}\text{N}_3$ ) at $\approx 137^\circ\text{C}$	hP12 $\text{P}6_322$ $\text{Mn}_{1.2}\text{N}_3$	a= 489.16 c= 455.45	[85Vil]; powder pattern: ASTM file card # 31-824
$\text{Mn}_2\text{N}_{0.60}$ (r) at RT	oP12 Pbcn $\text{PbQ}_2$	a= 453.7 b= 566.8 c= 490.9	[85Vil]
$\text{Mn}_2\text{N}$	oC24 $\text{C}222_1$ $\text{Mn}_2\text{N}$	a= 485.52 b= 840.88 c= 453.27	[85Vil]

Tab.22.1 continued:

$\eta$ - $\text{Mn}_3\text{N}_2$	tI10 I4mm $\text{Th}\bar{H}_2$ (L'2b)	a= 297.4 c= 1212.6	[84Jac]
$\theta$ - $\text{Mn}_3\text{N}_2$ (r) T<400	t**	a= 421.5 c= 414.5	[85Vil]; powder pattern: ASTM file card # 1-1158
$\theta$ - $\text{Mn}_3\text{N}_2$ (h) T>400	c**	a= 422.5	[85Vil]
Si	cF8 $\text{Fd}\bar{3}m$ C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ - $\text{Si}_3\text{N}_4$	hP28 P31c $\text{Si}_3\text{N}_4$	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ - $\text{Si}_3\text{N}_4$	hP14 $\text{P6}_3/m$ $\text{Si}_3\text{N}_4$	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160
* $\text{MnSiN}_2$	oP16 $\text{Pna}2_1$	a= 524.8 b= 651.1 c= 507.0	[85Vil]; powder pattern: ASTM file card # 25-548

Tab.22.2: Thermodynamic data for the solid phases in Mn - Si - N

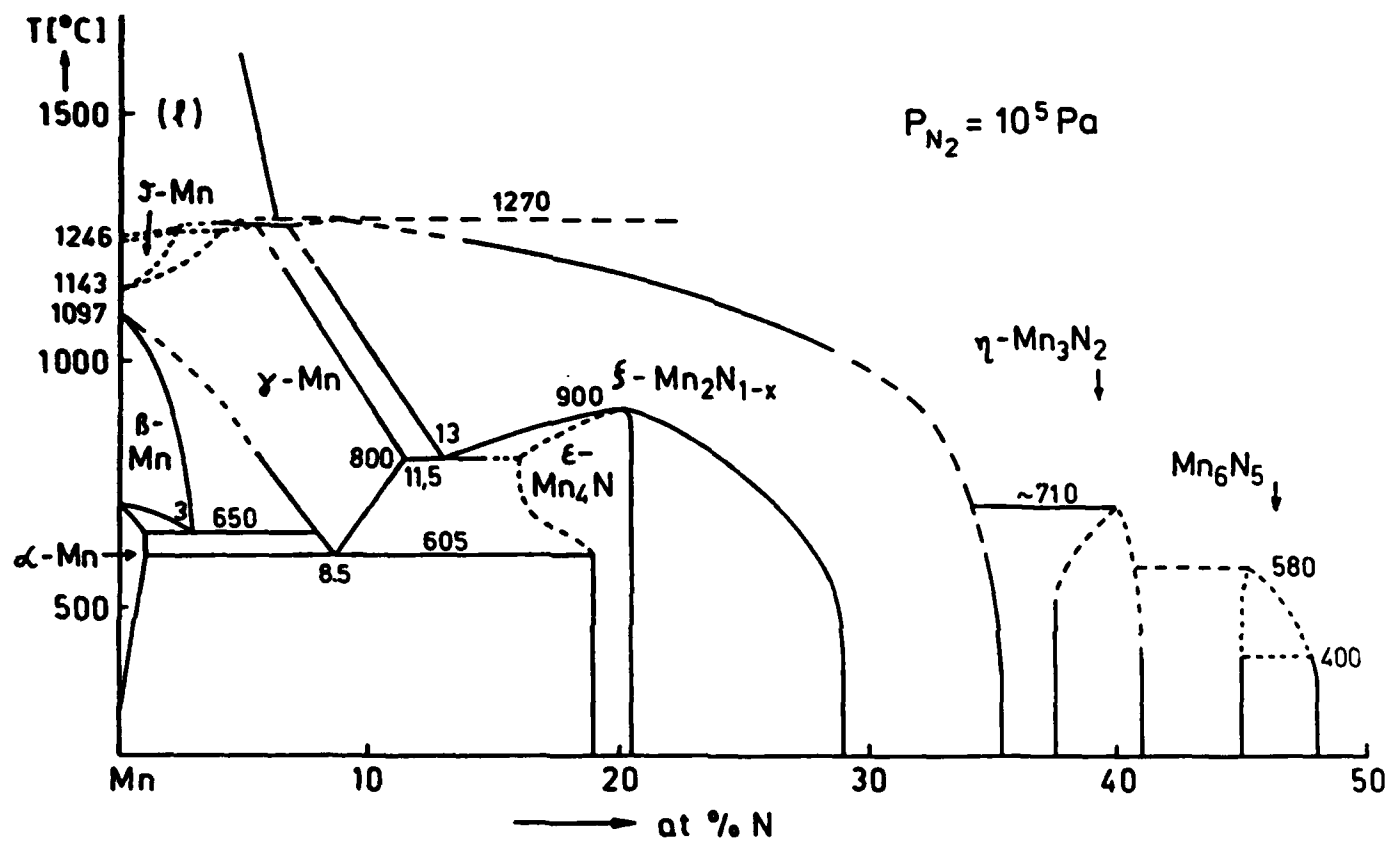
phase	$\Delta G_f^\circ$ [J/gramatom]	Comment
.1429 $\text{Si}_3\text{N}_4$	$-124602 + 57.95 \text{ T}$	[76Pro]
.0333 $\text{Mn}_3\text{Si}_{10}$	$-9661.5 + 1.0 \text{ T}$	[89Cha]
.5000 $\text{MnSi}$	$-12253.2 + 1.0 \text{ T}$	[89Cha]
.1250 $\text{Mn}_3\text{Si}_2$	$-12874.5 + 1.25 \text{ T}$	[89Cha]
.1429 $\text{Mn}_3\text{Si}_2$	$-11542.2 + 1.5 \text{ T}$	[89Cha]
.2500 $\text{Mn}_3\text{Si}$	$-10897.0 + 1.5 \text{ T}$	[89Cha]
.0909 $\text{Mn}_3\text{Si}_2$	$-8629.5 + 1.0 \text{ T}$	[89Cha]
.1429 $\text{Mn}_3\text{Si}$	$-7101.0 + 0.75 \text{ T}$	[89Cha]
$\beta$ -Mn(s.s.14at% Si)	-6000 (at 1273K)	estimated from plot $\Delta G_f^{1273}$ vs. $x_{\text{Si}}$
$\gamma$ -Mn(s.s.10at% N)	-2000 (at 1273K) (or more negative)	estimated from 1) $\text{Mn} + \epsilon\text{-Mn}_3\text{N} \xrightleftharpoons{773\text{K}} \gamma\text{-Mn}_3\text{N}_4$ 2) $T_{\text{decomp.}} = 1573\text{K}$ for $\gamma\text{-Mn}_3\text{N}_4$ at $p(\text{N}_2) = 10^5 \text{ Pa}$
.2000 $\epsilon\text{-Mn}_3\text{N}$	$-4534 + 3.266 \text{ T}$	calc. from data given in [75Gme]
.3333 $\zeta\text{-Mn}_3\text{N}$	$-83667.7 + 5.807 \text{ T}$	calc. from data given in [75Gme]
.2000 $\eta\text{-Mn}_3\text{N}_2$	$-6680 + 5.696 \text{ T}$	calc. from data given in [75Gme]
* .2500 $\text{MnSiN}_2$	$-42250 \pm 500$ (at 1273K)	estimated from the exp. obs. tie lines: 1) coex. ( $\text{Si}_3\text{N}_4 + \text{Mn}_3\text{Si}$ ) but <u>not</u> ( $\text{MnSiN}_2 + \text{Mn}_3\text{Si}_2$ ) 2) coex. ( $\text{MnSiN}_2 + \text{Mn}_3\text{Si}$ ) but <u>not</u> ( $\text{Si}_3\text{N}_4 + \text{Mn}_3\text{Si}_2$ ) or ( $\text{Si}_3\text{N}_4 + \beta\text{-Mn(s.s.Si)}$ ) resp.

Tab.22.3: Calculated invariant equilibria in Mn - Si - N at 1000°C

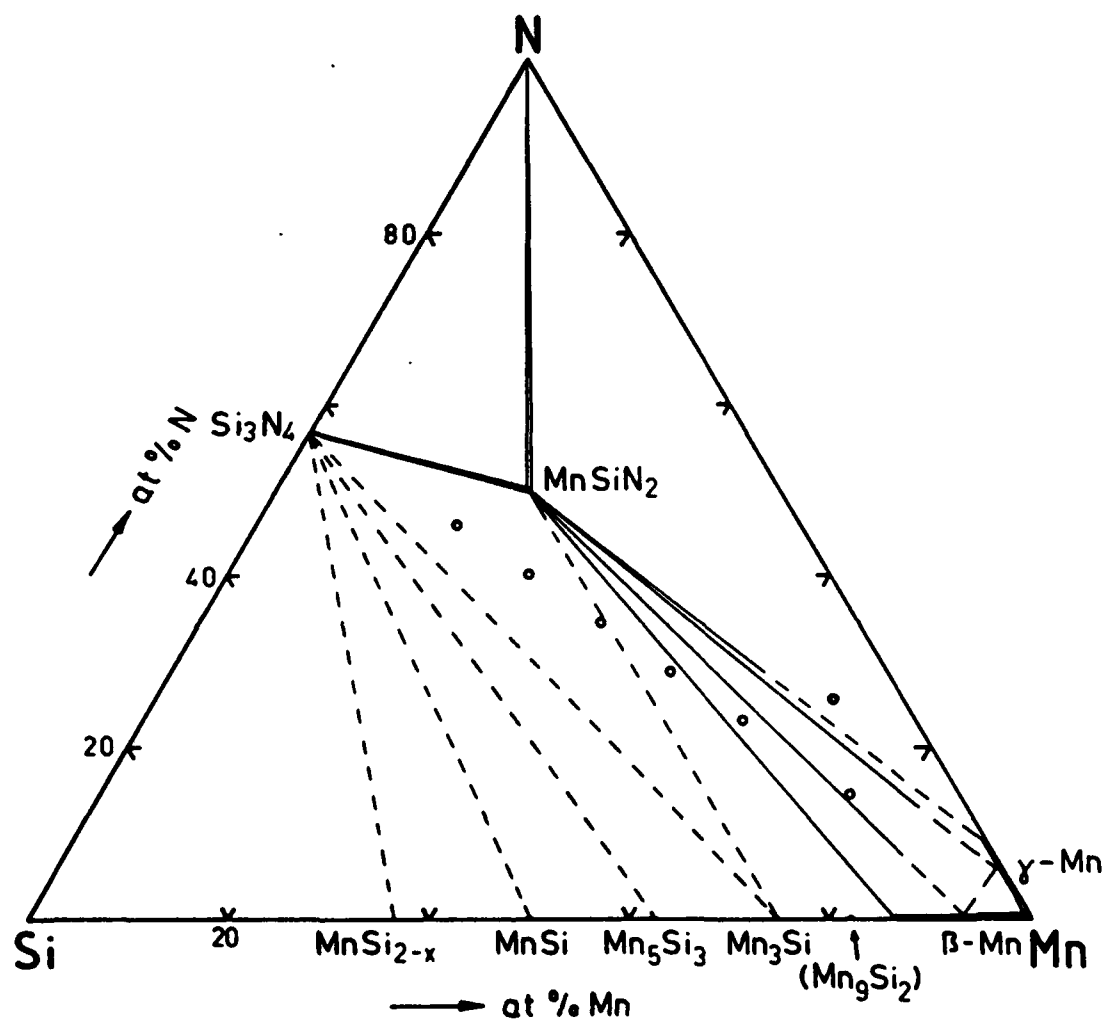
$p(N_2)$ (Pa)	Reaction
$5 \times 10^{-3}$	$Si_3N_4 = 3 Si + 2 N_2$
$6 \times 10^{-3}$	$Si_3N_4 + 8.278 Mn_{.5} Si_{.5} = 11.278 Mn_{.267} Si_{.622} + 2 N_2$
$20 \times 10^{-3}$	$Si_3N_4 + 12 Mn_{.625} Si_{.375} = 15 Mn_{.5} Si_{.5} + 2 N_2$
$130 \times 10^{-3}$	$Si_3N_4 + 15 Mn_{.75} Si_{.25} = 18 Mn_{.625} Si_{.375} + 2 N_2$
$180 \times 10^{-3}$	$MnSiN_2 = .222 Si_3N_4 + 1.333 Mn_{.75} Si_{.25} + .556 N_2$
$200 \times 10^{-3}$	$MnSiN_2 + 7.333 Mn_{.818} Si_{.182} = 9.333 Mn_{.75} Si_{.25} + N_2$
$330 \times 10^{-3}$	$MnSiN_2 + 15.217 \beta\text{-Mn (s.s.14at\% Si)} =$ $17.217 Mn_{.818} Si_{.182} + N_2$
max. 2875	$MnSiN_2 + 6.825 \gamma\text{-Mn (s.s.10at\% N)} =$ $7.143 \beta\text{-Mn (s.s.14at\% Si)} + 1.321 N_2$



Fig.22.1: Phase diagram of the boundary system manganese - nitrogen



**Fig.22.2: Isothermal section observed in the system Mn - Si - N  
at 1000°C (in the absence of external nitrogen pressure)**



## SYSTEM RHENIUM - SILICON - NITROGEN (Re-Si-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria of Re-Si-N between 1000°C and 1400°C were determined by x-ray analysis [88Sch]. The alloys investigated were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si, from Alpha Div., Ventron Corp., USA), silicon (purity: 3N, from Alpha Div., Ventron Corp., USA) and rhenium (purity: 4N, from Johnson, Mathey and Brandenberger, Switzerland). Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were either sealed in evacuated quartz tubes lined with Mo foil and heat treated for 400h at temperatures up to 1000°C or annealed in an r.f. furnace under argon (purity: 5N+) at temperatures up to 1400°C.

### BINARY SYSTEMS

The phase diagram for the binary system Re-Si due to [82Jor] is reproduced in [76Mof]. No phase diagram for the systems Re-N or Si-N is reported. It is likely, that the rhenium nitride reported to exist up to 370°C (tab.23.1) is stabilized by oxygen.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.23.1). The solubility of nitrogen in silicon as well as rhenium is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Re-Si-N (tab.23.1) Figs.23.1 and 23.2 show the phase equilibria in the absence of external nitrogen pressure at 1000°C and 1400°C resp. [88Sch]. At 1000°C  $\text{Si}_3\text{N}_4$  coexists with rhenium, but at 1400°C a three phase field  $\text{Si}_3\text{N}_4 + \text{Re}_{17}\text{Si}_6 + \text{N}_2(\text{gas})$  exists. Thus the onset for the decomposition of  $\text{Si}_3\text{N}_4$  by rhenium is between these temperatures. Lattice parameters of neither rhenium silicide coexisting with  $\text{Si}_3\text{N}_4$  or  $\text{N}_2$  gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in rhenium silicides.

Using the thermodynamic data in tab.23.2 the nitrogen pressures for the invariant equilibria occurring at 1000°C as well as at 1400°C are calculated (tab.23.3). The resulting tie lines are consistent with the experimentally observed isothermal sections (figs.23.1 and 23.2).

#### REFERENCES

- [73Cha] T.Chart, "Thermochemical Data for Transition Metal - Silicon Systems", High Temp. High Press. 5 (1973) 241-252
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [76Mof] W.Moffatt, "The Handbook of Binary Phase Diagrams", (General Electric Comp., Schenectady, NY., 1976 and updates)
- [82Jor] J.L.Jorda, M.Ishikawa and J.Muller, "Phase Relations and Superconductivity in the Binary Re-Si System ", J.Less.Common Met. 85 (1982) 27-35
- [83Haq] A.ul.Haq and O.Meyer, "Superconductivity and Electrical Properties of Rhenium Nitride Prepared by Ion Implantation", J.Low Temp.Phys. 50 (1983) 123-133
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [88Sch] J.C.Schuster, "Silicon Nitride - Metal Joints: Phase Equilibria in the Systems Si<sub>3</sub>N<sub>4</sub> - Cr, Mo, W and Re", J.Mater.Sci. 23 (1988) 2792-2796

Table 23.1: Solid phases in the system Re - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Re	hP2 P6 <sub>3</sub> /mmc Mg (A3)	a= 276.09 c= 445.76	[85Vil];powder pattern: ASTM file card # 5-702
Re <sub>17</sub> Si <sub>6</sub> (Re <sub>5</sub> Si <sub>3</sub> )	mP24 P2 <sub>1</sub> /b	a= 645.11 b= 960.12 c= 539.38 $\beta = 94.2^\circ$	[85Vil];powder pattern: ASTM file card # 32-891
ReSi T>1650	cP8 P2 <sub>1</sub> 3 FeSi (B20)	a=477.5	[85Vil];powder pattern: ASTM file card # 8-278
ReSi <sub>2</sub>	oI6 Immm	a= 312.8 b= 314.4 c= 767.7	[85Vil];powder pattern: ASTM file card # 35-1384
ReN <sub>1-x</sub>	cF8 Fm $\bar{3}$ m NaCl (defect)	a= 402	[83Haq];gives powder pattern
Si	cF8 Fd $\bar{3}$ m C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

Tab.23.2: Thermodynamic data for the solid phases in Re - Si - N

phase	$\Delta G_f^\circ$ [J/gramatom]	Comment
.1429 $\text{Si}_3\text{N}_4$	$-124602 + 57.95 \text{ T}$	[76Fro]
.3333 $\text{ReSi}_2$	$-30100 + 0.0 \text{ T}$	[73Cha]
.5000 $\text{ReSi}$	$-26400 + 0.0 \text{ T}$	[73Cha]
.1250 $\text{Re}_5\text{Si}_3$	$-19700 - 2.1 \text{ T}$	[73Cha]
(~.0385 $\text{Re}_{17}\text{Si}_6$ )		

Tab.23.3: Calculated invariant equilibria in Re - Si - N

a) at 1000°C (1273K):

$p(\text{N}_2)$ (Pa)	Reaction
$5 \times 10^{-3}$	$\text{Si}_3\text{N}_4 = 3 \text{ Si} + 2 \text{ N}_2$
1.3	$\text{Si}_3\text{N}_4 + 3.429 \text{ Re}_{.025}\text{Si}_{.375} = 6.429 \text{ Re}_{.333}\text{Si}_{.667} + 2 \text{ N}_2$
24	$\text{Si}_3\text{N}_4 + 5 \text{ Re} = 8 \text{ Re}_{.025}\text{Si}_{.375} + 2 \text{ N}_2$

b) at 1400°C (1673K)

$p(\text{N}_2)$ (Pa)	Reaction
95	$\text{Si}_3\text{N}_4 = 3 \text{ Si} + 2 \text{ N}_2$
$5.8 \times 10^3$	$\text{Si}_3\text{N}_4 + 3.429 \text{ Re}_{.025}\text{Si}_{.375} = 6.429 \text{ Re}_{.333}\text{Si}_{.667} + 2 \text{ N}_2$
$76.2 \times 10^3$	$\text{Si}_3\text{N}_4 + 5 \text{ Re} = 8 \text{ Re}_{.025}\text{Si}_{.375} + 2 \text{ N}_2$

**Fig.23.1: Isothermal section observed in the system Re - Si - N  
at 1000°C (in the absence of external nitrogen pressure)**

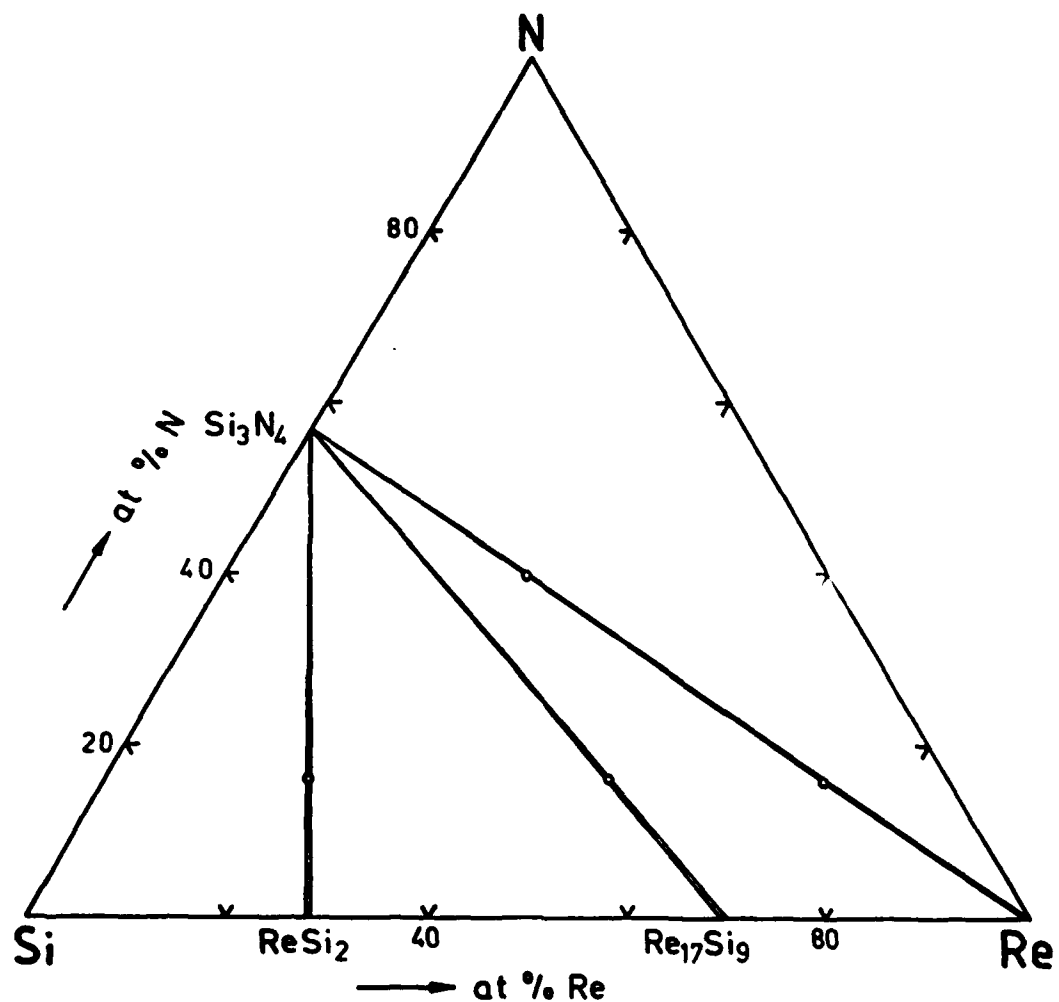
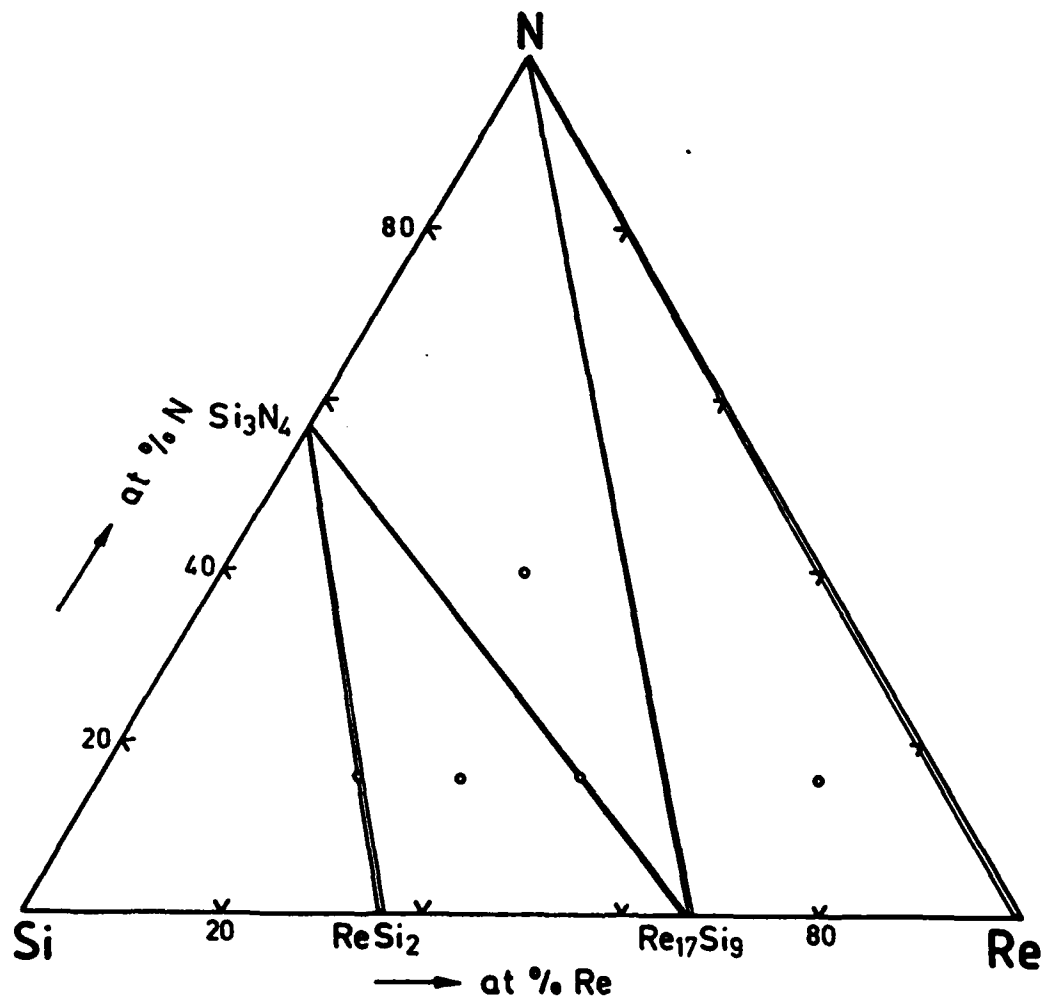


Fig.23.2: Isothermal section observed in the system Re - Si - N  
at 1400°C (under argon)





## SYSTEM IRON - SILICON - NITROGEN (Fe-Si-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria of Fe-Si-N between 900°C and 1150°C were determined by x-ray analysis [87Wei]. The alloys investigated were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si, from Alpha Div., Ventron Corp., USA), silicon (purity: 3N, from Alpha Div., Ventron Corp., USA) and iron (purity: 2N5, impurities in ppm: Ni 600, C < 600, O < 2000; from Fluka AG, Switzerland). Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were sealed in evacuated quartz tubes lined with Mo foil, heat treated either at 900°C, 340h or 1150°C, 170h and quenched.

### BINARY SYSTEMS

The phase diagram for the system Fe-Si given in [86Mas] is based on [80Sch]. However, according to more recent data [89Hil] no  $\alpha_2\text{-Fe}_3\text{Si}(h)$  exists (fig. 24.1). The phase diagram for the system Fe-N is given in [86Mas]. No phase diagram for the system Si-N is reported.  $\text{Si}_3\text{N}_4$  occurs in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ . Crystal structure data for the solid phases are listed in tab. 24.1. The solubility of nitrogen in silicon is very low [76Pro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Fe-Si-N (tab. 24.1). Two isothermal sections are reported [87Wei]: In the absence of external nitrogen partial pressure  $\text{Si}_3\text{N}_4$  is found to coexist at 900°C with all binary silicides stable at this temperature and with  $\alpha\text{-Fe}$  (fig. 24.2). At 1150°C  $\text{Si}_3\text{N}_4$  coexists with all stable binary silicides but is decomposed by iron forming  $\alpha\text{-Fe}$  containing  $7 \pm 1$  at% Si in solid solution (fig. 24.3). Under pure argon the onset of this decomposition reaction is observed at  $1120 \pm 10^\circ\text{C}$  [87Wei]. This agrees with earlier, just qualitative observations [57Gle][66Mue][66Yas][67Cal][69Fel][76Mat] and is consistent with [75Sie]. Lattice parameters of neither iron

silicide coexisting with  $\text{Si}_3\text{N}_4$  or  $\text{N}_2$  gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in iron silicides. The solid solution of 6 at% Si in  $\alpha$ -Fe, heat treated in a nitrogen atmosphere (95%  $\text{N}_2$ , 5%  $\text{H}_2$ ,  $P_{\text{total}}: 10^5$  Pa), dissolves  $2 \times 10^{-7}$  at% nitrogen at 900°C and  $1.3 \times 10^{-6}$  at% nitrogen at 1150°C resp. [63Pea].

## MISCELLANEOUS

Joining of  $\text{Si}_3\text{N}_4$  to steel by hot pressing resulted in excellent bonding due to the formation of iron silicides in the interface. However, due to thermal expansion mismatch low tensile strength (failure in the  $\text{Si}_3\text{N}_4$ ) resulted [88Sug]. Thus additional interlayers of other metals are preferred.

Iron is often used as addition in silicon to aid nitridation by promoting the formation of liquid phase at temperatures far below the melting point of pure Si [81Muk][81Shi]. The reaction products found are  $\text{Si}_3\text{N}_4$  and iron silicides [75Lei][85Bou], which however are recognized to be the primary cause of strength degradation in hot pressed silicon nitride [85Her].

Wetting angles under vacuum between  $\text{Si}_3\text{N}_4$  and  $\text{Fe}_2\text{Si}_5$  as well as FeSi are reported to be  $\theta = 66^\circ$  (at 1450°C) and  $\theta = 76^\circ$  (at 1500°C) respectively [73Cha].

Tennenhouse et al. [85Ten] investigated the interaction of  $\text{Si}_3\text{N}_4$  cutting tools with iron and iron based alloys in air. They conclude that the low melting phase formed during machining is an oxide phase and does not occur in the ternary Fe-Si-N.

## REFERENCES

- [57Gle] O. Glemser, K. Beltz and P. Naumann, "Investigation of the System Silicon - Nitrogen", *Z. Anorg. Allg. Chem.* 291 (1957) 50-66
- [63Pea] M. L. Pearce, "The Analysis and Solubility of Nitrogen in Silicon-Iron", *Trans. Met. Soc. AIME* 227 (1963) 1393-1400
- [66Mue] K. Müller and H. Rebsch, "Silicon Nitride - Corrosion Resistant and Stable Against Aluminium", *Silikattechnik* 17 (1966) 279-282

- [66Yas] G.A.Yasinskaya, "Wettability of Refractory Carbide, Boride and Nitride by Molten Metal", *Poroshk.Met.* 7 (1966) 53-56
- [67Cal] C.A.Calow and R.B.Barclay, "Observations on Whisker Stability in Metal Matrices", *J.Mater.Sci.* 2 (1967) 404-406
- [69Fel] H.Feld, E.Gugel and H.G.Nitzsche, "Silicon Nitride - A Corrosion Resistant High Temperature Material", *Werkstoffe Korros.* 20 (1969) 571-574
- [73Cha] J.A.Champion, B.J.Keene and S.Allen, "Wetting of Refractory Materials by Molten Metallides", *J.Mater.Sci.* 8 (1973) 423-426
- [75Lei] G.Leimer and E.Gugel, "Infiltration Composites Based on Silicon Nitride", *Z.Metallk.* 66 (1975) 570-576
- [75Sie] D.Sienel, "Sintered Iron Alloys by In Situ Decomposition of  $\text{CrSi}_2$ ,  $\text{Si}_3\text{N}_4$  and  $\text{Cr}_2\text{N}$  in Iron Powder", Report KfK # 2147 (Ges.f.Kernforschung GmbH., Karlsruhe, FRG, 1975) p53-56
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [76Mat] S.Matsumoto, Y.Kuranari, K.Maeda and S.Inamoto, " $\text{Si}_3\text{N}_4$ -Fe Alloy", *Jap.Kokai* 76.133 198 (1976)
- [80Sch] E.Schürmann and U.Hensgen, "Investigations of Melt Equilibria in the System Iron - Silicon", *Arch.Eisenhüttenw.* 51 (1980) 1-4
- [81Muk] J.Mukerji and S.K.Biswas, "Effect of Iron, Titanium and Hafnium on the Second Stage Nitriding of Silicon", *J.Amer.Ceram.Soc.* 64 (1981) 549-552
- [81Shi] S.Shinozaki and M.E.Milberg, "Electron Microscopy Study of the Effect of Iron in Reaction Sintered Silicon Nitride", *J.Amer.Ceram.Soc.* 64 (1981) 382-385
- [85Bou] C.E.Bouldin, E.A.Stern, M.S.Donley and T.G.Stoebe, "Iron Impurities in  $\text{Si}_3\text{N}_4$  Processing", *J.Mater.Sci.* 20 (1985) 1807-1814
- [85Her] L.Hermansson, J.Adlerborn and M.Burström, "Strength Controlling Defects in HIP-ed Silicon Nitride", *Rev.Chim.Miner.* 22 (1985) 467-472
- [85Ten] G.J.Tennenhouse, A.Ezis and F.D.Runkle, "Interaction of Silicon Nitride and Metal Surfaces", *J.Amer.Ceram.Soc.* 68 (1985) C30-C31
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [87Wei] F.Weitzer and J.C.Schuster, "Phase Diagrams of the Ternary Systems Mn, Fe, Co, Ni-Si-N", *J.Solid State Chem.* 70 (1987) 178-184
- [88Sug] K.Suganuma, Y.Miyamoto and M.Koizumi, "Joining of Ceramics and Metals", *Ann.Rev.Mater.Sci.* 18 (1988) 47-73
- [89Hil] K.Hilfrich, W.Kölker, W.Petry, O.Schärpf and E.Nembach, "Revision of the Fe-rich Section of the Fe-Si Phase Diagram", Poster at Hauptversammlung Deutsche Ges.f.Metallk., Karlsruhe, FRG, 1989.

Table 24.1: Solid phases in the system Fe - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\alpha$ -Fe(r) T<911	cI2 Im $\bar{3}$ m W (A2)	a= 286.65	[85Vil];powder pattern: ASTM file card # 6-696
$\gamma$ -Fe(h) 911<T<1392	cF4 Fm $\bar{3}$ m Cu (A1)	a= 366.60	[85Vil];powder pattern: ASTM file card # 31-619
Fe <sub>3</sub> Si	cF16 Fm $\bar{3}$ m BiF <sub>3</sub> (DO <sub>3</sub> )	a= 560.8	[85Vil];powder pattern: ASTM file card # 11-616
Fe <sub>2</sub> Si T>1044	hP6 P $\bar{3}$ m1	a= 405.2 c= 508.55	[85Vil];
Fe <sub>3</sub> Si <sub>2</sub> 825<T<1056	hP16 P6 <sub>3</sub> /mcm Mn <sub>3</sub> Si <sub>2</sub> (D8 <sub>3</sub> )	a= 675.52 c= 471.74	[85Vil];powder pattern: ASTM file card # 38-438
FeSi	cP8 P2 <sub>1</sub> 3 FeSi (B20)	a= 448.91	[85Vil];powder pattern: ASTM file card # 38-1397
FeSi <sub>2</sub> (r) T<986	oC48 Cmca	a= 986.3 b= 779.1 c= 783.3	[85Vil];powder pattern: ASTM file card # 20-532
FeSi <sub>2</sub> (h) (Fe <sub>2</sub> Si <sub>3</sub> ) T>955	tP3 P4/mmm	a= 269.5 c= 509.0	[85Vil];powder pattern: ASTM file card # 22-1113 35-822
Fe <sub>4</sub> N T<680	cP5 Pm $\bar{3}$ m Fe <sub>4</sub> N (L'1)	a= 379.70	[85Vil];powder pattern: ASTM file card # 6-627
$\epsilon$ -Fe <sub>3</sub> N T<500	hP3 P6 <sub>3</sub> /mmc Fe <sub>3</sub> N (L'3)	a= 270.5 c= 437.6	[85Vil]powder pattern: ASTM file card # 1-1236 3-925

Tab.24.1 cont.

Si	cF8 Fd $\bar{3}m$ C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>2</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160

Fig.24.1: Phase diagram of the boundary system iron - silicon

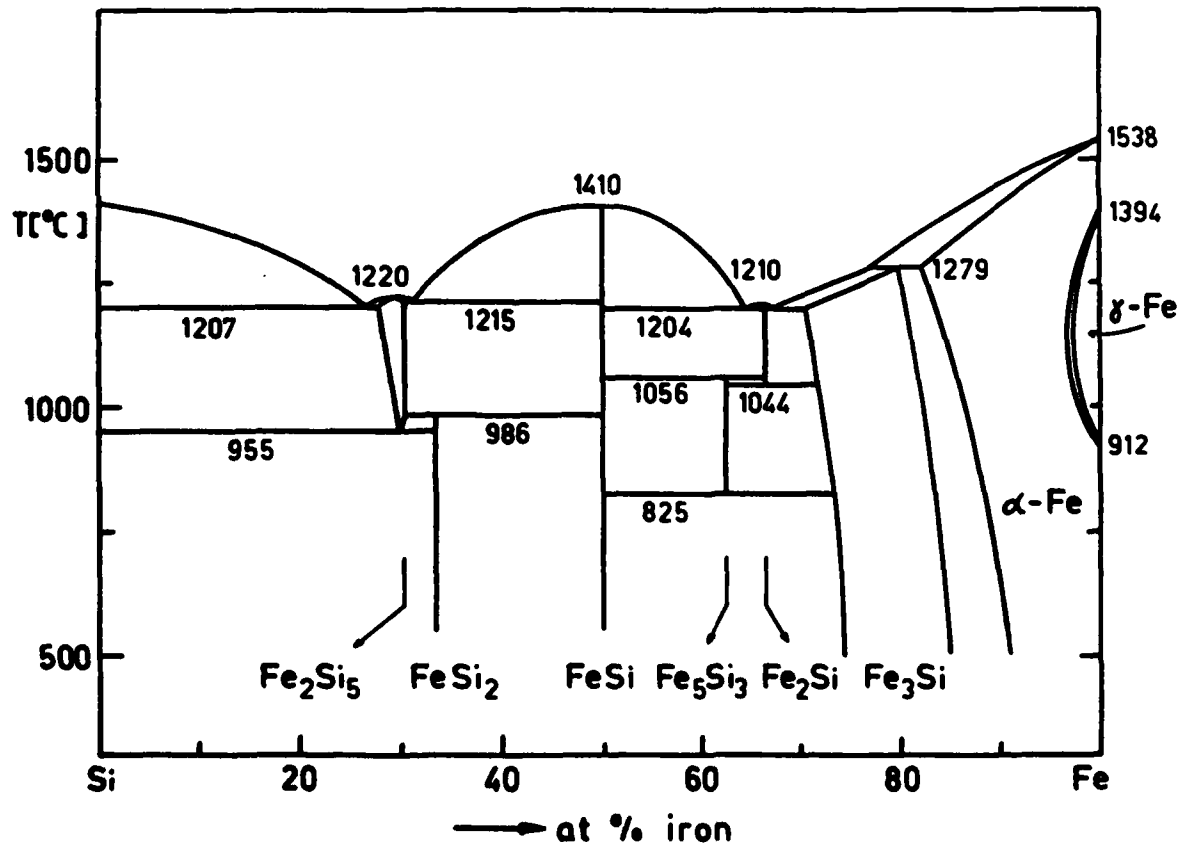
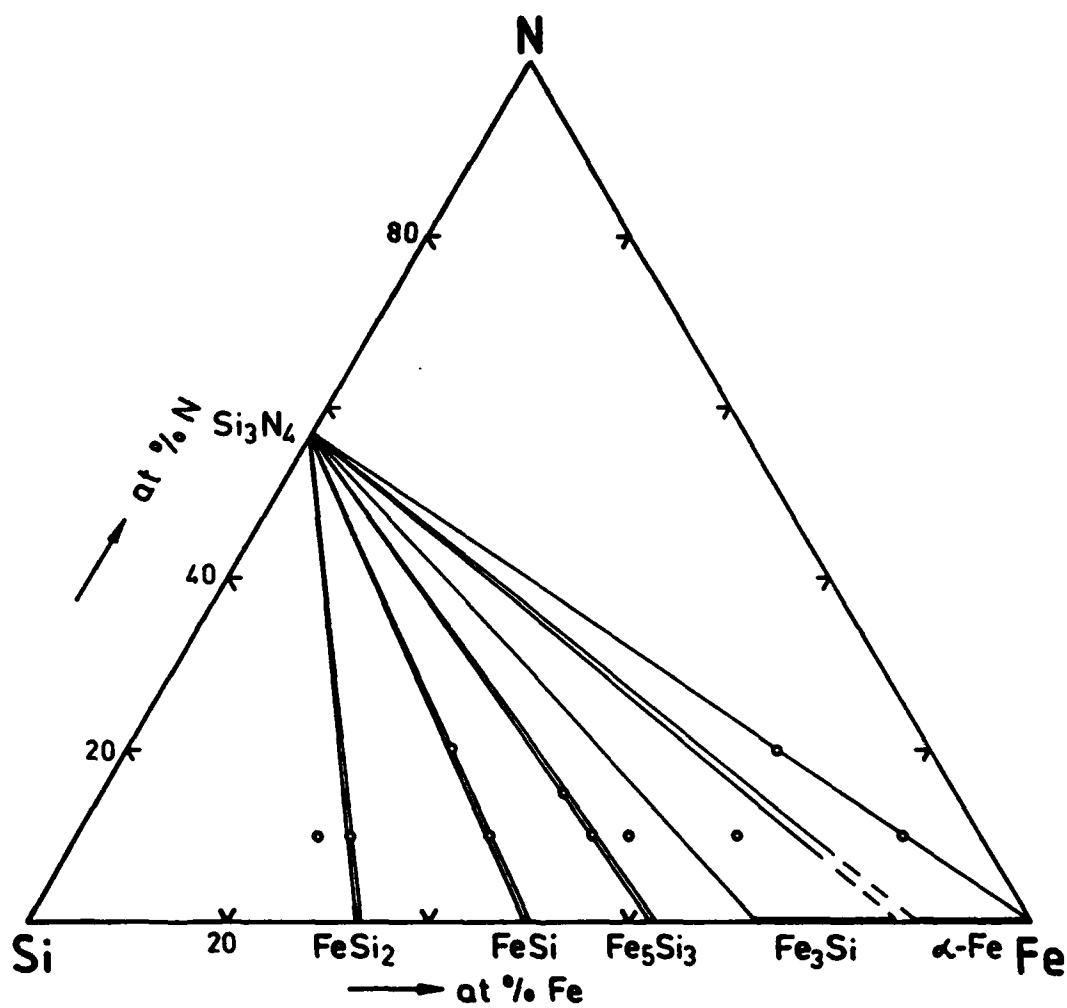
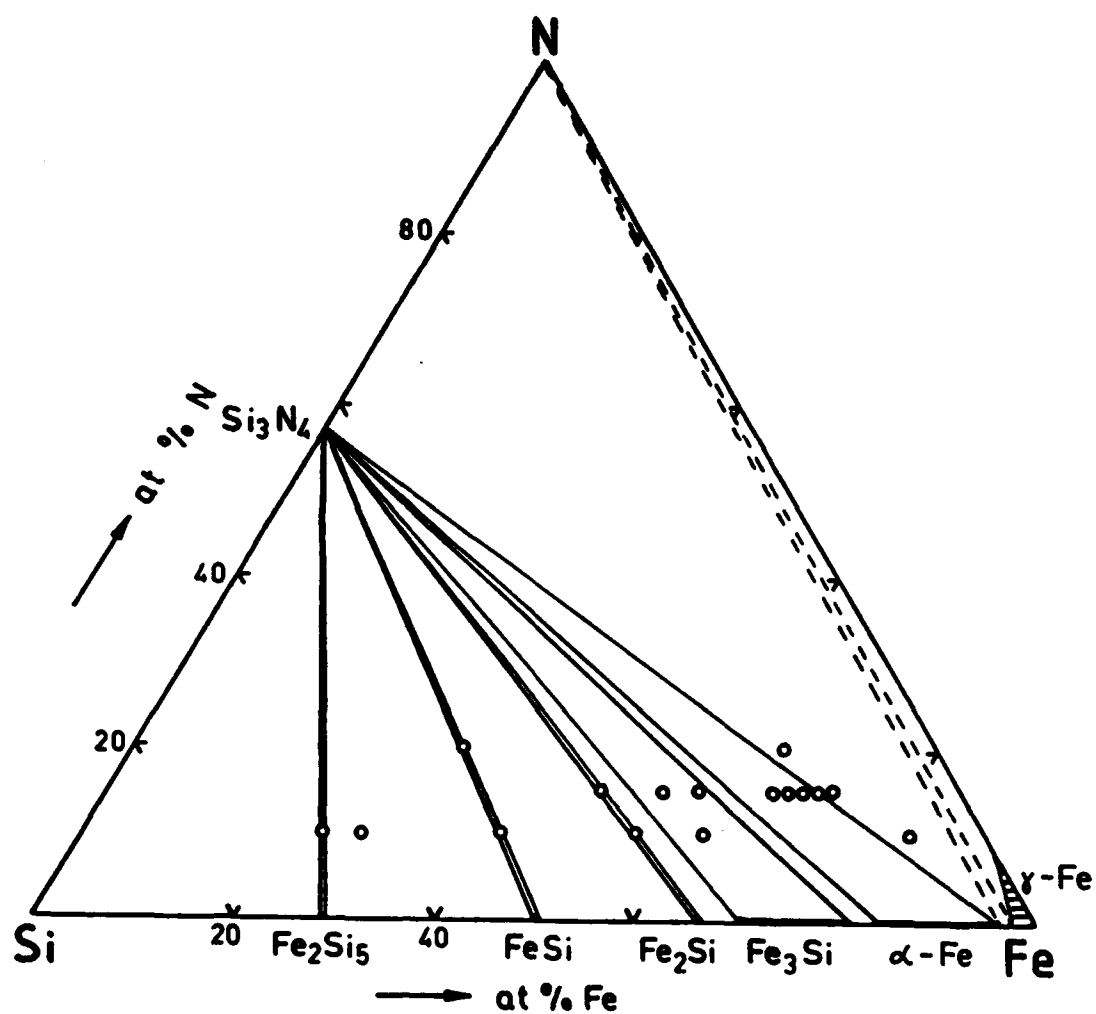


Fig.24.2: Isothermal section observed in the system Fe - Si - N  
at 900°C (in the absence of external nitrogen pressure)



**Fig.24.3: Isothermal section observed in the system Fe - Si - N  
at 1150°C (in the absence of external nitrogen pressure)**



## SYSTEM RUTHENIUM - SILICON - NITROGEN (Ru-Si-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria of Ru-Si-N at 1000°C and 1250°C were determined by x-ray analysis [88Wei]. The alloys investigated were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si, from Alpha Div., Ventron Corp., USA), silicon (purity: 3N, from Alpha Div., Ventron Corp., USA) and ruthenium (purity: 3N, from Engelhard Ind. Div., USA). Mixtures of these powders and/or of powdered master alloys made thereof by arc melting were cold pressed and annealed in evacuated quartz tubes lined with Mo foil at 1000°C (170h) and 1100°C (up to 500h) followed by water quench. Heat treatments at higher temperatures (up to 1330°C, 72h) were conducted in alumina crucibles placed in an rf-furnace under  $10^{-5}$  Pa high purity (5N) argon. Gas quenching after rf-treatment can be considered moderate only.

### BINARY SYSTEMS

The phase diagram for the binary system Ru-Si (fig.25.1) was redetermined by [88Wei]. No phase diagrams for the systems Ru-Si or Si-N resp. are reported.  $\text{Si}_3\text{N}_4$  occurs in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ . Crystal structure data for the solid phases are listed in tab.25.1. The solubility of nitrogen in silicon as well as in ruthenium is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Ru-Si-N (tab.25.1). Two isothermal sections are reported [88Wei]: In the absence of external nitrogen partial pressure  $\text{Si}_3\text{N}_4$  is found to coexist at 1000°C with all binary silicides stable at this temperature and with Ru (fig.25.2). At 1250°C  $\text{Si}_3\text{N}_4$  coexists with  $\text{Ru}_2\text{Si}_3$  and RuSi but is decomposed by alloys more rich in ruthenium (fig.25.3). Under pure argon the onset of this decomposition reaction is observed at  $1210 \pm 10^\circ\text{C}$  [88Wei]. Lattice parameters of neither ruthenium silicide coexisting with  $\text{Si}_3\text{N}_4$  or  $\text{N}_2$  gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in ruthenium silicides.



# REFERENCES

- [76Fro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [85Vil] P. Villars and L.D. Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, OH., 1985)
- [88Wei] F. Weitzer, P. Rogl and J.C. Schuster, "X-Ray Investigations in the Systems Ruthenium-Silicon and Ruthenium-Silicon-Nitrogen", Z. Metallk. 79 (1988) 154-156

Fig.25.1: Phase diagram of the boundary system Ru - Si

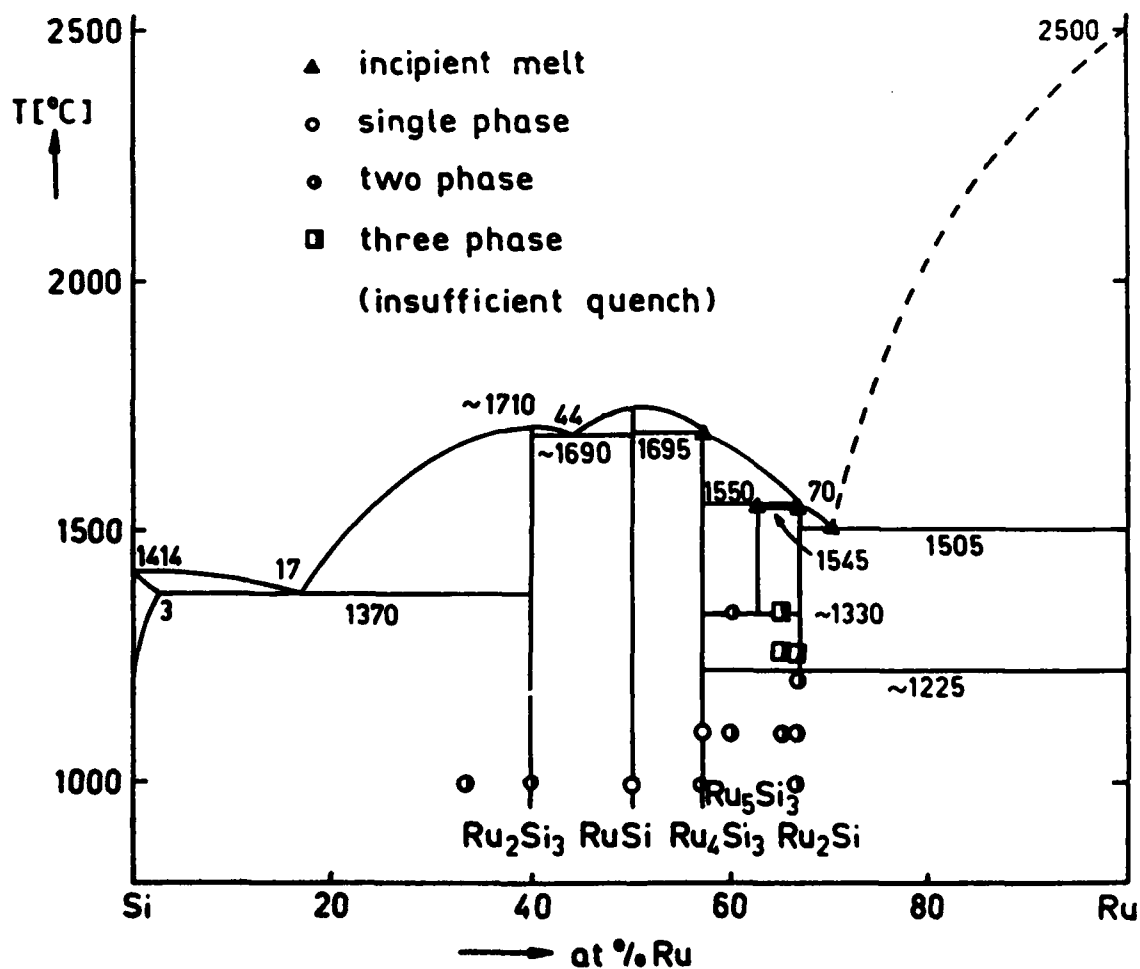
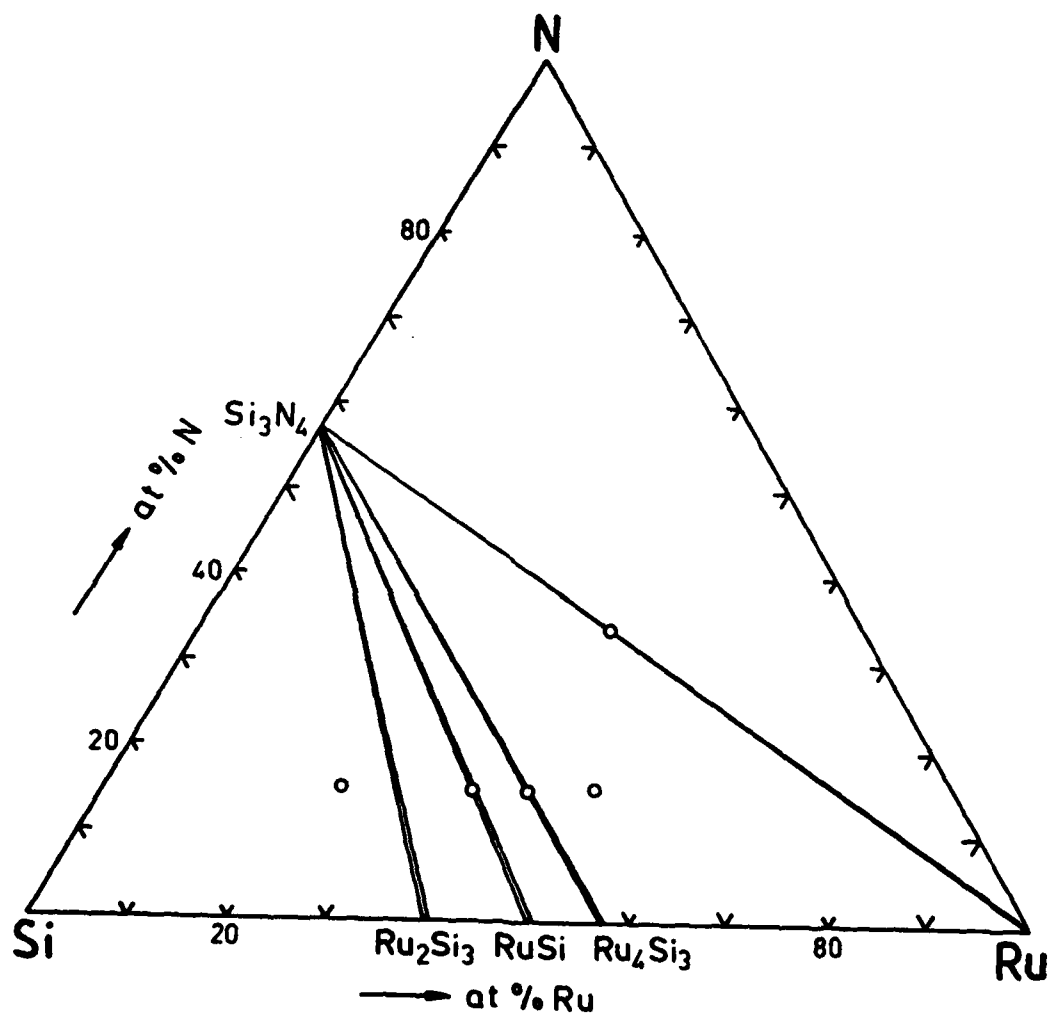


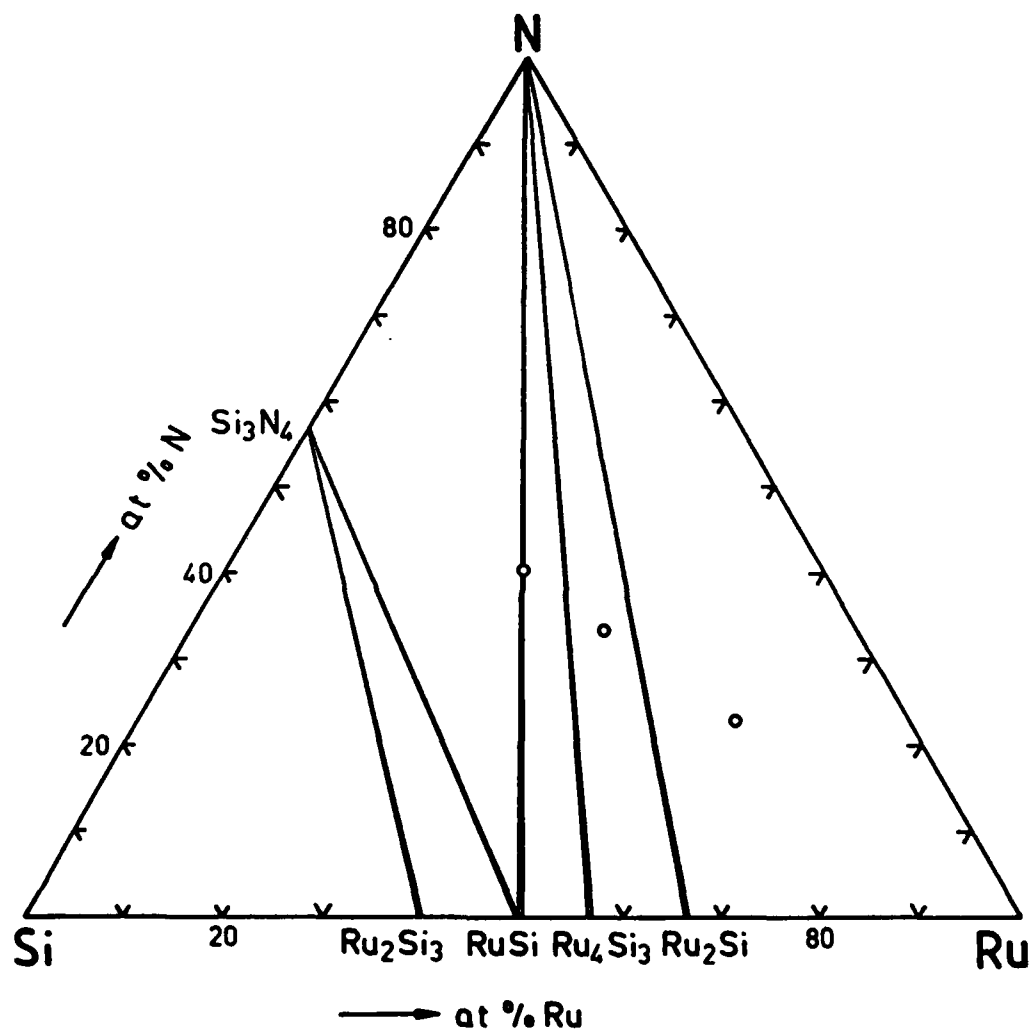
Table 25.1: Solid phases in the system Ru - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Ru	hP2 P6 <sub>3</sub> /mmc W (A2)	a= 270.0 c= 427.5	[85V11]; powder pattern: ASTM file card # 6-663
Ru <sub>2</sub> Si 1255<T<1505	oP12 Pnma C <sub>2</sub> Si (C23)	a= 527.9 b= 400.5 c= 741.8	[85V11]; powder pattern: ASTM file card # 14-334
Ru <sub>3</sub> Si <sub>2</sub> 1330<T<1550	oP16 Pbam Rh <sub>3</sub> Ge <sub>2</sub>	a= 524.6 b= 981.5 c= 402.3	[85V11];
Ru <sub>4</sub> Si <sub>3</sub>	oP28 Pnma Rh <sub>4</sub> Si <sub>3</sub>	a= 519.36 b= 402.16 c= 1734.3	[85V11];
RuSi (Ru rich)	cP2 Pm $\bar{3}$ m CsCl (B1)	a= 290.9	[85V11]; powder pattern: ASTM file card # 10-213
RuSi (Ru poor)	cP8 P <sub>2</sub> 3 FeSi (B20)	a= 470.3	[85V11]; powder pattern: ASTM file card # 18-1140
Ru <sub>2</sub> Si <sub>3</sub>	tP80 P $\bar{4}$ c2 Ru <sub>2</sub> Sn <sub>3</sub>	a= 1107.5 c= 895.4	[85V11]; powder pattern: ASTM file card # 32-978
Si	cF8 Fd $\bar{3}$ m C (A4)	a= 357.1 b= 357.1 c= 357.1	[85V11]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85V11]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85V11]; powder pattern: ASTM file card # 29-1132 33-1160

Fig.25.2: Isothermal section observed in the system Ru - Si - N  
at 1000°C (in the absence of external nitrogen pressure)



**Fig.25.3: Isothermal section observed in the system Ru - Si - N  
at 1250°C (under argon)**



## SYSTEM COBALT - SILICON - NITROGEN (Co-Si-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria of Co-Si-N between 1000°C were determined by x-ray analysis [87Wei]. The alloys investigated were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si, from Alpha Div., Ventron Corp., USA), silicon (purity: 3N, from Alpha Div., Ventron Corp., USA) and cobalt (purity: 2N8, impurities in ppm: Fe<500, Ni<500, Mn<50, Cu<50; from Fluka AG, Switzerland). Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were sealed in evacuated quartz tubes lined with Mo foil, heat treated at 1000°C, 170h and quenched.

### BINARY SYSTEMS

The phase diagram for the binary system Co-Si in [86Mas] is a reproduction of [58Han], the Co rich section of which needs to be modified (fig.26.1) according to [72Boo] and [73Koe]. No phase diagrams are reported for the systems Co-N or Si-N. None of the cobalt nitrides reported (tab.26.1) is stable at 1000°C,  $p(\text{N}_2) \leq 10^5 \text{ Pa}$  [87Wei].  $\text{Si}_3\text{N}_4$  occurs in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ . Crystal structure data for the solid phases are listed in tab.26.1. The solubility of nitrogen in silicon as well as in cobalt is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Co-Si-N (tab.26.1). In the absence of external nitrogen partial pressure  $\text{Si}_3\text{N}_4$  is found to coexist at 1000°C with all binary silicides stable at this temperature and with  $\alpha\text{-Co}$  (fig.26.2). Under pure argon the onset of the decomposition of  $\text{Si}_3\text{N}_4$  in contact with Co is observed at 1170°C [87Wei]. This agrees with earlier, just qualitative observations [66Mue][66Yas]. Lattice parameters of neither cobalt silicide coexisting with  $\text{Si}_3\text{N}_4$  or  $\text{N}_2$  gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in cobalt silicides.

Using the thermodynamic data in tab.26.2 the nitrogen pressures for the invariant equilibria occurring at 1000°C are calculated (tab.26.3). The resulting tie lines are consistent with the observed isothermal sections (figs.26.2).

#### MISCELLANEOUS

Wetting angles of the silicides CoSi and "Co<sub>2</sub>Si" on Si<sub>3</sub>N<sub>4</sub> are reported to be  $\theta = 62^\circ$  and  $\theta = 40^\circ$  resp. under vacuum [73-1Cha].

#### REFERENCES

- [58Han] M.Hansen, "Constitution of Binary Alloys" (McCraw Hill, New York, USA, 1958)
- [66Mue] K.Müller and H.Rebsch, "Silicon Nitride - Corrosion Resistant and Stable Against Aluminium", Silikattechnik 17 (1966) 279-282
- [66Yas] G.A.Yasinskaya, "Wettability of Refractory Carbide, Boride and Nitride by Molten Metal", Poroshk.Met. 7 (1966) 53-56
- [72Boo] J.van den Boomgaard and F.M.A.Carpay, "The Eutectoid Co<sub>2</sub>Si Phase in the Co-Si System", Acta Met. 20 (1972) 473-473
- [73-1Cha] J.A.Champion, B.J.Keene and S.Allen, "Wetting of Refractory Materials by Molten Metallides", J.Mater.Sci. 8 (1973) 423-426
- [73-2Cha] T.Chart, "Thermochemical Data for Transition Metal - Silicon Systems", High Temp.High Press. 5 (1973) 241-252
- [73Koe] W.Köster, H.Warlimont and T.Gödeke, "The System Cobalt-Co<sub>2</sub>Si", Z.Metallk. 64 (1973) 399-405
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [84Pas] A.Pasturel, P.Hicter and F.Cyrot-Lackmann, "On the Heats of Formation of Solid Germanides and Silicides of Transition Metals", Physica 124B (1984) 247-250
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [87Wei] F.Weitzer and J.C.Schuster, "Phase Diagrams of the Ternary Systems Mn, Fe, Co, Ni-Si-N", J.Solid State Chem. 70 (1987) 178-184

Table 26.1: Solid phases in the system Co - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\alpha$ -Co(h) T>410	cF4 Fm $\bar{3}$ m Cu (A1)	a= 354.46	[85Vil]; powder pattern: ASTM file card # 15-806
$\epsilon$ -Co(r) T<410	hP2 P6 <sub>3</sub> /mmc Mg (A3)	a= 250.71 c= 406.95	[85Vil]; powder pattern: ASTM file card # 5-727
Co <sub>3</sub> Si(h) 1193<T<1214	t**	a= 842 c= 581	[85Vil];
Co <sub>2</sub> Si(r) T<1238	oP12 Pnma Co <sub>2</sub> Si (C23)	a= 491.8 b= 373.8 c= 710.9	[85Vil]; powder pattern: ASTM file card # 4-847
Co <sub>2</sub> Si(h) T>1238			
CoSi	cP8 P2 <sub>1</sub> 3 FeSi (B20)	a= 444.26	[85Vil]; powder pattern: ASTM file card # 8-362
CoSi <sub>2</sub>	cF12 Fm $\bar{3}$ m CaF <sub>2</sub> (C1)	a= 536.5	[85Vil]; powder pattern: ASTM file card # 8-344 38-1449
Co <sub>4</sub> N	c**	a= 373.8	[85Vil]
Co <sub>3</sub> N	hP*	a= 274.6 c= 432.2	[85Vil]; powder pattern: ASTM file card # 6-691
Co <sub>2</sub> N	oP6 Pnnm Fe <sub>2</sub> C	a= 460.56 b= 434.43 c= 285.35	[85Vil]; powder pattern: ASTM file card # 6-647

Tab.26.1 continued

Si	cF8 Fd $\bar{3}m$ C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160

Tab.26.2: Thermochemical data for the solid phases in Co - Si - N

phase	$\Delta G_f^\circ$ [J/gramatom]	Comment
.1429 Si <sub>3</sub> N <sub>4</sub>	-124602 + 57.95 T	[76Fro]
.3333 CoSi <sub>2</sub>	-32900 + 1.2 T	[73-2Cha]
.5000 CoSi	-47500 - 3.1 T	[73-2Cha]
.3333 Co <sub>2</sub> Si(r)	-37700 - 0.0 T	[73-2Cha]
.2500 Co <sub>3</sub> Si	$\Delta H_f^{298} = -28450$	[84Pas]



Tab.26.3: Calculated invariant equilibria in Co - Si - N at 1000°C

$P(N_2)$ (Pa)	Reaction
$5 \times 10^{-3}$	$Si_3N_4 = 3 Si + 2 N_2$
$14 \times 10^{-3}$	$Si_3N_4 + 6 Co_{.5}Si_{.5} = 9 Co_{.333}Si_{.667} + 2 N_2$
29.3	$Si_3N_4 + 9 Co_{.667}Si_{.333} = 12 Co_{.5}Si_{.5} + 2 N_2$
.....	$Si_3N_4 + 12.275 \epsilon-Co(s.s.17at\% Si) =$ $15.275 Co_{.667}Si_{.333} + 2 N_2$
.....	$Si_3N_4 + 264 \alpha-Co(s.s.11at\% Si) =$ $267 \epsilon-Co(s.s.12at\% Si) + 2 N_2$

Fig.26.1: Phase diagram of the boundary system Co - Si

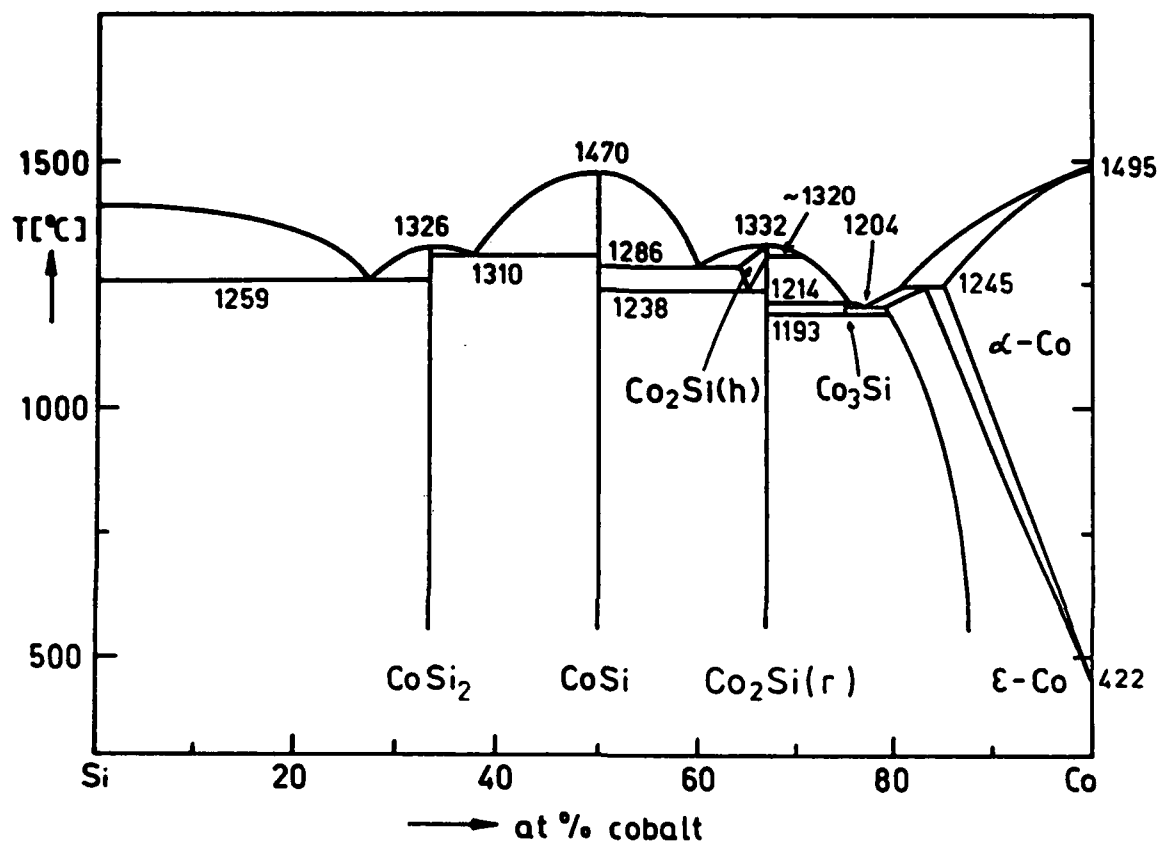
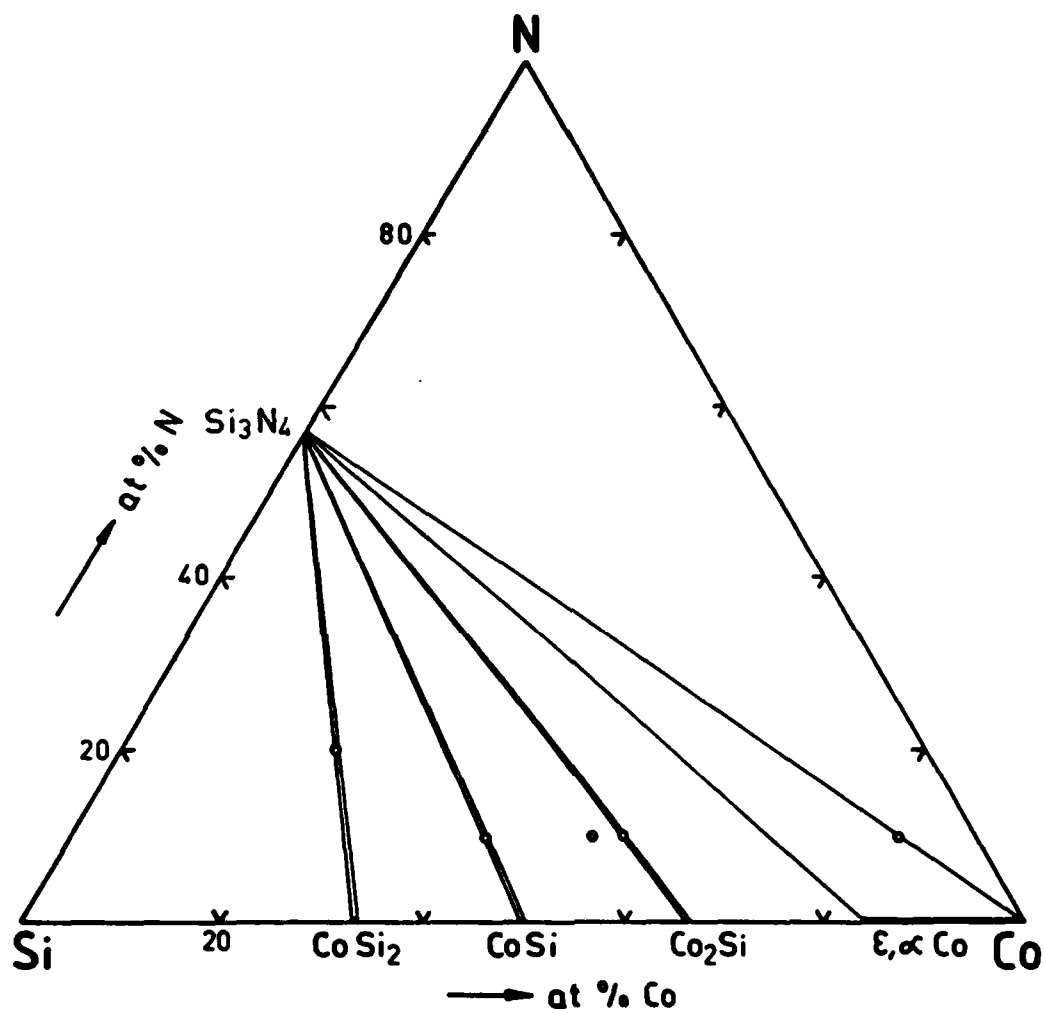


Fig.26.2: Isothermal section observed in the system Co - Si - N  
at 1000°C (in the absence of external nitrogen pressure)



## SYSTEM RHODIUM - SILICON - NITROGEN (Rh-Si-N)

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### INTRODUCTION/EXPERIMENTAL

An isothermal section is derived for 1250°C. Two ternary alloys were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si), silicon (purity: 3N), both from Alpha Div., Ventron Corp., USA and rhodium (purity: 3N; from Degussa, FRG). Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were heat treated at 1250°C, 72h in alumina crucibles placed in an rf-furnace under  $10^{-5}$  Pa high purity (5N) argon. Gas quenching after rf-treatment can be considered moderate only.

### BINARY SYSTEMS

The phase diagram for the system Rh-Si due to [85Sch] is reproduced in [76Mof]. Structural data for the intermediate phases are listed in tab. 27.1. No phase diagrams are reported for the systems Rh-N or Si-N.  $\text{Si}_3\text{N}_4$  occurs in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ . Crystal structure data for the solid phases are listed in tab. 27.1. The solubility of nitrogen in silicon as well as rhodium is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Rh-Si-N (tab. 27.1). At 1250°C three rhodium silicides are stable (fig. 27.1). Under argon  $\text{Si}_3\text{N}_4$  is found to coexist at this temperature with RhSi but not with  $\text{Rh}_2\text{Si}_3$ ,  $\text{Rh}_2\text{Si}$  or rhodium (fig. 27.2). In accordance with the rather moderate quenching rate RhSi(x) rather than RhSi(h) is observed.

### REFERENCES

- [76Fro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [76Mof] G. Moffatt, "The Handbook of Binary Phase Diagrams", (General Electric Comp., NY., Schenectady, 1976 and updates)
- [85Sch] L. Schellenberg, J. Jorda and J. Muller, "The Rhodium-Silicon Phase Diagram", J. Less common Met. 109 (1985) 261-274

Tab.27.1: Solid phases in the system Rh - Si - N

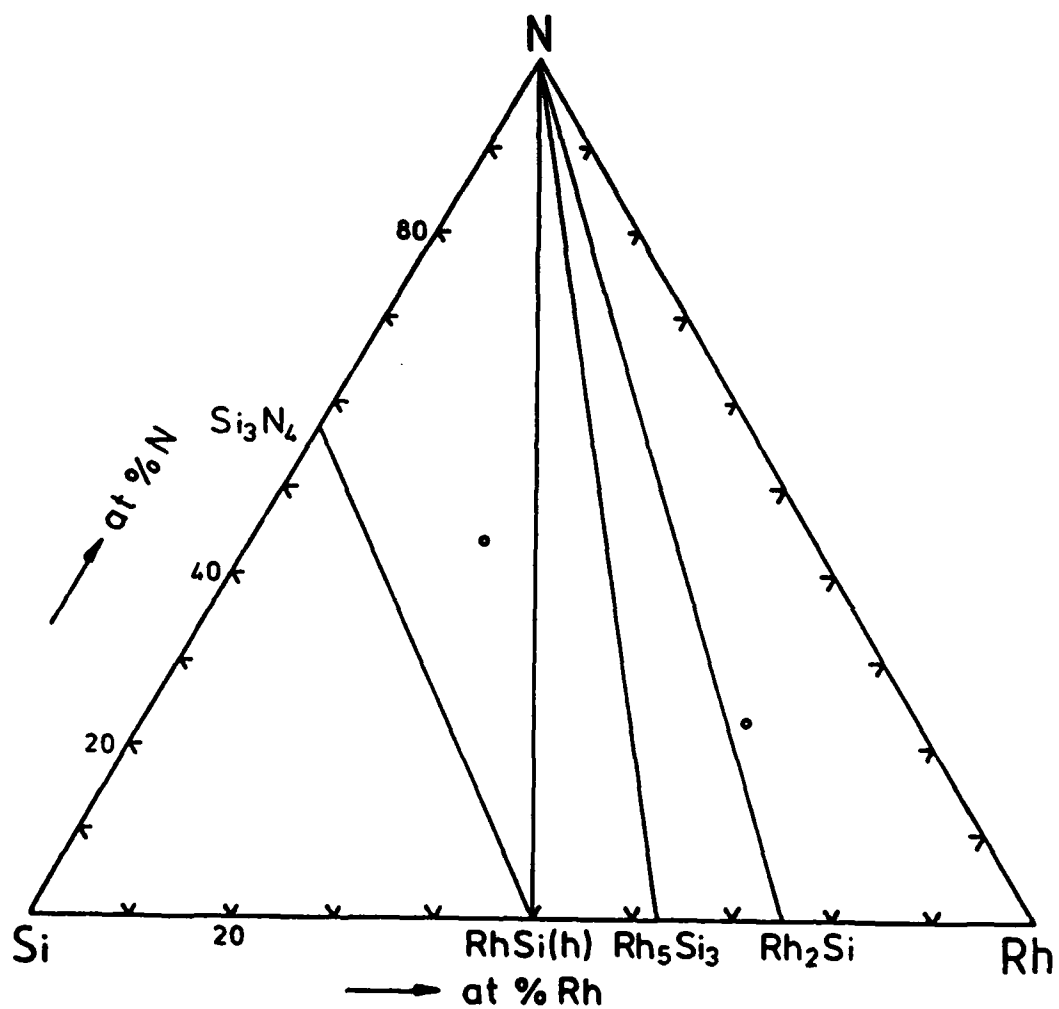
Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Rh	cF4 Fm $\bar{3}$ m Cu (A1)	a= 380.34	[85Vil];powder pattern: ASTM file card # 5-685
Rh <sub>2</sub> Si	oP12 Pnma Cq <sub>2</sub> Si (C23)	a= 540.8 b= 393 c= 738.3	[85Vil];powder pattern: ASTM file card # 37-1316
Rh <sub>3</sub> Si <sub>2</sub>	oP16 Pbam Rh <sub>3</sub> Ge <sub>2</sub>	a= 531.7 b= 1013.1 c= 389.5	[85Vil];powder pattern: ASTM file card # 37-1317
Rh <sub>20</sub> Si <sub>13</sub> 1050<T<1225	hP34 P6 <sub>3</sub> /m	a= 1185.1 c= 362.3	[85Vil];powder pattern: ASTM file card # 37-1318
Rh <sub>2</sub> Si <sub>2</sub> T<820	hP6 P6 <sub>3</sub> /mmc InNi <sub>2</sub> (B8 <sub>2</sub> )	a= 394.2 c= 504.7	[85Vil];powder pattern: given in [85Sch]
RhSi(h) T>1030 (Rh rich)	cP8 P2 <sub>1</sub> 3 FeSi (B20)	a= 467.4	[85Vil]
RhSi(x)	mP* P2 <sub>1</sub> /c	a= 458.8 b= 456.8 c= 553.6 $\beta$ = 115.92	martens.transf. RhSi(h) [85Sch];powder pattern: ASTM file card # 38-999
RhSi(r) T<1080 (Si rich)	oP8 Pnma MnP (B31)	a= 553.1 b= 306.3 c= 636.2	[85Vil];powder pattern: ASTM file card # 35-1075
Rh <sub>2</sub> Si <sub>3</sub>	mP18 P2 <sub>1</sub> /m Rh <sub>2</sub> Si <sub>3</sub>	a= 1233.5 b= 350.8 c= 592.4 $\beta$ = 100.18	[85Vil];powder pattern: ASTM file card # 35-1076
Rh <sub>3</sub> Si <sub>4</sub>	oP28 Pnma Rh <sub>3</sub> Si <sub>4</sub>	a= 1881.0 b= 361.4 c= 581.3	[85Vil];powder pattern: ASTM file card # 35-1077

Tab.27.1 continued

Si	CF8 Fd3m C (A4)	a= 542.86	[85V11]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85V11]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85V11]; powder pattern: ASTM file card # 29-1132 33-1160

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Fig.27.1: Isothermal section observed in the system Rh - Si- N  
at 1250°C (under argon)



## SYSTEM NICKEL - SILICON - NITROGEN (Ni-Si-N)

### INTRODUCTION / EXPERIMENTAL

Phase equilibria of Ni-Si-N at 900°C were determined by x-ray analysis [87Wei]. The alloys investigated were prepared using powders of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si), silicon (purity: 3N) and nickel (purity: 3N) all from Alpha Div., Ventron Corp., USA. Cold pressed mixtures of these powders and/or of powders of master alloys made thereof were sealed in evacuated quartz tubes lined with Mo foil, heat treated at 900°C, 340h and quenched.

### BINARY SYSTEMS

The phase diagrams for the binary systems Ni-Si as well as Ni-N are given in [86Mas]. The system Ni-Si was thermodynamically modelled [86Mey], [87Mey]. No phase diagram for the system Si-N is reported.  $\text{Si}_3\text{N}_4$  occurs in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ . Crystal structure data for the solid phases are listed in tab.28.1. The solubility of nitrogen in silicon as well as nickel is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase exists in Ni-Si-N (tab.28.1). In the absence of external nitrogen partial pressure  $\text{Si}_3\text{N}_4$  is found to coexist at 900°C with all binary silicides stable at this temperature and with Ni (fig.28.1). Under pure argon the onset of the decomposition of  $\text{Si}_3\text{N}_4$  by nickel is observed at  $1170 \pm 10^\circ\text{C}$  [87Wei]. This agrees with earlier, just qualitative observations [66Mue][66Yas][69Fel][79Ben] and is consistent with [89Bri]. Lattice parameters of neither nickel silicide coexisting with  $\text{Si}_3\text{N}_4$  or  $\text{N}_2$  gas are altered with respect to the values of the pure binary alloys indicating virtual insolubility of nitrogen in nickel silicides.

Using the thermodynamic data in tab.28.2 the nitrogen pressures for the invariant equilibria occurring at 900°C are calculated



(tab.28.3). The resulting tie lines are consistent with the observed isothermal section (figs.28.1)

#### MISCELLANEOUS

The wetting angle under vacuum between  $\text{Si}_3\text{N}_4$  and  $\text{Ni}_2\text{Si}$  is reported to be  $\theta = 108^\circ$  (at  $1450^\circ\text{C}$ ) [73Cha].

#### REFERENCES

- [39Osa] A.Osawa and M.Okamoto, "An X-ray Analysis of Alloys in the Nickel-Silicon System", Sci.Rep.Tohoku Univ. 27 (1939) 326-345
- [66Mue] K.Müller and H.Rebsch, "Silicon Nitride - Corrosion Resistant and Stable Against Aluminium", Silikattechnik 17 (1966) 279-282
- [66Yas] G.A.Yasinskaya, "Wettability of Refractory Carbide, Boride and Nitride by Molten Metal", Poroshk.Met. 6 (1966) 53-56
- [69Fel] H.Feld, E.Gugel and H.G.Nitzsche, "Silicon Nitride - A Corrosion Resistant High Temperature Material", Werkstoffe Korros. 20 (1969) 571-574
- [73Cha] J.A.Champion, B.J.Keene and S.Allen, "Wetting of Refractory Materials by Molten Metallides", J.Mater.Sci. 8 (1973) 423-426
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [79Ben] M.J.Bennett and M.R.Houlton, "The Interaction Between Silicon Nitride and Several Iron, Nickel and Molybdenum Alloys", J.Mater.Sci. 14 (1979) 184-196
- [79Ell] M.Ellner, S.Heinrich, M.K.Bhargava and K.Schubert, "Structural Investigations in the Alloy  $\text{NiSi}_3$ ", J.Less Common Met. 66 (1979) 163-173
- [83Dor] G.J.W.R.Dorman and M.S.Sikkens, "Structure of Reactively Sputtered Nickel Nitride Films", Thin Solid Films 105 (1983) 251-258
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [86Mey] S.an Mey, "A Thermodynamic Evaluation of the Ni-Si System", Z.Metallk. 77 (1986) 805-810
- [87Mey] S.an Mey, "Note on the Evaluation of the Ni-Si System", private communication, 1987
- [87Wei] F.Weitzer and J.C.Schuster, "Phase Diagrams of the Ternary Systems Mn, Fe, Co, Ni-Si-N", J.Solid State Chem. 70 (1987) 178-184
- [89Bri] M.E.Brito, H.Yokoyama, Y.Hirotsu and Y.Mutoh, "High Resolution and Analytical Electron Microscopy Study of  $\text{Si}_3\text{N}_4$ -Ni Bonded Interface", Iron Steel Inst.Jap.Int. 29 (1989) 253-258

Table 28.1: Solid phases in the system Ni - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Ni	CF4 Fm $\bar{3}$ m Cu (Al)	a= 352.32	[85Vil]; powder pattern: ASTM file card # 4-850
Ni <sub>3</sub> Si(r) (Ni <sub>20</sub> Si <sub>6</sub> ) T<1031	CP4 Fm $\bar{3}$ m Cu <sub>3</sub> Au (L1 <sub>2</sub> )	a= 350.4	[85Vil]; powder pattern: given in [390sa]
Ni <sub>3</sub> Si(h) 1114<T<1164	CP2 Pm $\bar{3}$ m	a= 280.8	[85Vil];
Ni <sub>3</sub> Si(h) (Ni <sub>25</sub> Si <sub>6</sub> ) 987<T<1114	hP*	a= 669.8 c= 2885.5	cited as Ni <sub>27</sub> Si <sub>13</sub> in [85Vil] powder pattern: in [79E11]
Ni <sub>31</sub> Si <sub>12</sub> (Ni <sub>5</sub> Si <sub>2</sub> )	hP43 P321 Ni <sub>31</sub> Si <sub>12</sub>	a= 667.1 c= 1228.8	[85Vil]; powder pattern: ASTM file card # 17-222 24-524
Ni <sub>2</sub> Si(r) T<1217	oP12 Pnma Cq <sub>2</sub> Si (C23)	a= 500 b= 373 c= 704	[85Vil]; powder pattern: ASTM file card # 3-943
Ni <sub>2</sub> Si(h) (Ni <sub>3</sub> Si <sub>2</sub> (h)) T>806	hP6 P6 <sub>3</sub> /m	a= 380.5 c= 489.0	[85Vil]; powder pattern: ASTM file card #3-1069
Ni <sub>3</sub> Si <sub>2</sub> (r) T<843	oC80 Cmc2 <sub>1</sub> Ni <sub>3</sub> Si <sub>2</sub>	a= 1222.9 b= 1080.5 c= 692.4	[85Vil]; powder pattern: ASTM file card # 17-881
NiSi	oP8 Pnma MnP (B31)	a= 518 b= 334 c= 562	[85Vil]; powder pattern: ASTM file card # 38-844
NiSi <sub>2</sub>	cF12 Fm $\bar{3}$ m CaF <sub>2</sub> (C1)	a= 540.6	[85Vil]; powder pattern: given in [390sa]

Tab.28.1 continued

$\text{Ni}_3\text{N}$	CP5 $\text{Pm}\bar{3}\text{m}$ $\text{Fe}_3\text{N}$ (L'1)	a= 374.0	[85Vil];powder pattern: ASTM file card # 36-1300
$\text{Ni}_3\text{N}$	t**	a= 372 c= 728	[85Vil];powder pattern: given in [83Dor]
$\text{Ni}_3\text{N}$ T<400 in $\text{N}_2$	hP* P6 <sub>3</sub> 22 or P312	a= 460.7 c= 430.4	[85Vil];powder pattern: ASTM file card # 10-280
Si	cF8 $\text{Fd}\bar{3}\text{m}$ C (A4)	a= 542.86	[85Vil];powder pattern: ASTM file card # 5-565
$\alpha\text{-Si}_3\text{N}_4$	hP28 P31c $\text{Si}_3\text{N}_4$	a= 781.8 c= 559.1	[85Vil];powder pattern: ASTM file card # 9-250
$\beta\text{-Si}_3\text{N}_4$	hP14 P6 <sub>3</sub> /m $\text{Si}_3\text{N}_4$	a= 760.8 c= 291.1	[85Vil];powder pattern: ASTM file card # 29-1132 33-1160

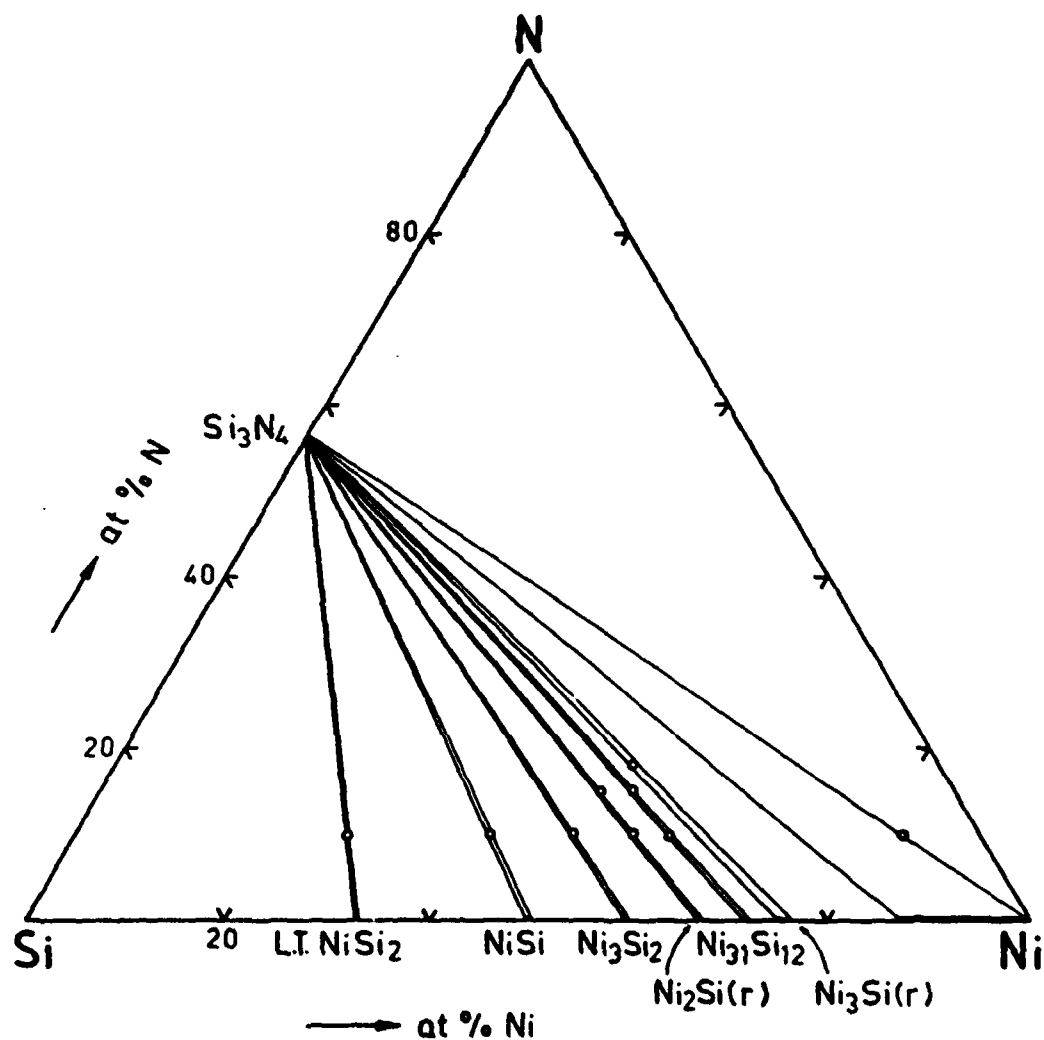
Tab.28.2: Thermochemical data for the solid phases in Ni - Si - N

phase	$\Delta G_f^\circ$ [J/gramatom]	Comment
.1429 $\text{Si}_3\text{N}_4$	$-124602 + 57.95 T$	[76Fro]
.3333 $\text{NiSi}_2(\text{r})$	$-36159.2 + 154.02 T - 25.02 T \ln T - .00185 T^2 + 180498/T$	[86Mey]
.5000 $\text{NiSi}$	$-42442.1 + 145.95 T - 24.38 T \ln T - .00153 T^2 + 162967/T$	[86Mey]
.2000 $\text{Ni}_2\text{Si}_3(\text{r})$	$-45996.1 + 146.93 T - 24.55 T \ln T - .00222 T^2 + 116002/T$	[87Mey]
.3333 $\text{Ni}_2\text{Si}(\text{h})$	$-45666.1 + 146.28 T - 24.71 T \ln T - .00292 T^2 + 69036/T$	[86Mey]
for $x_{\text{Si}} = 0.4$ :	$-81000$ (at 1173K)	(estimated from plot $\Delta G_f^{1173}$ vs. $x_{\text{Si}}$ )
.3333 $\text{Ni}_2\text{Si}(\text{r})$	$-47668.2 + 132.10 T - 22.19 T \ln T - .00486 T^2 + 69036/T$	[87Mey]
.1429 $\text{Ni}_3\text{Si}_2$ ( $\text{Ni}_{31}\text{Si}_{12}$ )	$-49358.8 + 149.68 T - 24.76 T \ln T - .00303 T^2 + 60407/T$	[86Mey]
.2500 $\text{Ni}_3\text{Si}(\text{h}')$	$-47801.4 + 150.00 T - 24.81 T \ln T - .00313 T^2 + 51777/T$	[86Mey]
( $\text{Ni}_{25}\text{Si}_9$ )		
.2500 $\text{Ni}_3\text{Si}(\text{h})$	$-42985.5 + 146.55 T - 24.81 T \ln T - .00313 T^2 + 51777/T$	[86Mey]
.2500 $\text{Ni}_3\text{Si}(\text{r})$	$-49261.6 + 151.64 T - 24.81 T \ln T - .00313 T^2 + 51777/T$	[86Mey]
( $\text{Ni}_{20}\text{Si}_8$ )		
$\text{Ni}(\text{s.s.12at\% Si})$	$-76000$ (at 1173K)	(estimated from plot $\Delta G_f^{1173}$ vs. $x_{\text{Si}}$ )

Tab.28.3: Calculated invariant equilibria in Ni - Si - N at 900°C

$p(\text{N}_2)$ (Pa)	Reaction
$0.15 \times 10^{-3}$	$\text{Si}_3\text{N}_4 = 3 \text{ Si} + 2 \text{ N}_2$
.16	$\text{Si}_3\text{N}_4 + 6 \text{ Ni}_{.5}\text{Si}_{.5} = 9 \text{ Ni}_{.333}\text{Si}_{.667} + 2 \text{ N}_2$
.2	$\text{Si}_3\text{N}_4 + 15 \text{ Ni}_{.6}\text{Si}_{.4}(\text{h}) = 18 \text{ Ni}_{.5}\text{Si}_{.5} + 2 \text{ N}_2$
1.6	$\text{Si}_3\text{N}_4 + 27 \text{ Ni}_{.667}\text{Si}_{.333}(\text{r}) = 30 \text{ Ni}_{.6}\text{Si}_{.4}(\text{h}) + 2 \text{ N}_2$
77	$\text{Si}_3\text{N}_4 + 36.855 \text{ Ni}_{.721}\text{Si}_{.279} =$ $39.855 \text{ Ni}_{.667}\text{Si}_{.333}(\text{r}) + 2 \text{ N}_2$
$6.7 \times 10^3$	$\text{Si}_3\text{N}_4 + 51.216 \text{ Ni}_{.763}\text{Si}_{.237} =$ $54.219 \text{ Ni}_{.721}\text{Si}_{.279} + 2 \text{ N}_2$
$9 \times 10^3$	$\text{Si}_3\text{N}_4 + 19.564 \text{ Ni}(\text{s.s.12at\%Si}) =$ $22.564 \text{ Ni}_{.763}\text{Si}_{.237} + 2 \text{ N}_2$

Fig.28.1: Isothermal section observed in the system Ni - Si - N  
at 900°C (in the absence of external nitrogen pressure)



## SYSTEM COPPER - SILICON - NITROGEN (Cu-Si-N)

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### INTRODUCTION / EXPERIMENTAL

The phase equilibria of Cu-Si-N at 700°C were determined by X-ray analysis [90Wei]. The 8 alloys investigated were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ ; 58 at% Si; from Alpha Div., Ventron Corp., USA) and Cu or arc melted Cu-Si alloys resp. (Cu powder, 3N, from E. Merck A.G., FRG; Cu rods, 5N+, from Ventron GmbH, FRG; Si powder, m4N, from Fluka AG, Buchs, Switzerland).

### BINARY SYSTEMS

The phase diagram for the system Cu-Si is given in [86Mas]. No phase diagrams exist in the literature for Cu-N and Si-N. In the system Cu-N three intermediate phases are reported to exist: The most stable of these,  $\text{Cu}_3\text{N}$  (tab. 29.1), decomposes around/above 310°C (in hydrogen atmosphere) [84Bai]. Two azides,  $\text{CuN}_3$  and  $\text{Cu}_2\text{N}_3$ , were synthesized at room temperature [48Wil], [68Soe]. Silicon nitride exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab. 29.1). The solubility of nitrogen in copper as well as in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Cu-Si-N at 700°C (tab. 29.1). Fig. 29.1 shows the isothermal section at 700°C in the absence of external nitrogen pressure. Cu as well as all binary Cu-silicides stable at 700°C coexist with  $\text{Si}_3\text{N}_4$ . This is in agreement with earlier data [69Fel], [75Lei]. Lattice parameter measurements indicate insolubility of nitrogen in Cu or any of the Cu silicides nor of Cu in  $\text{Si}_3\text{N}_4$ .

### MISCELLANEOUS

Liquid copper does not wet  $\text{Si}_3\text{N}_4$  ( $\theta = 144 \pm 10^\circ$  under vacuum [66Yas], [66Mue], [87Nak], [Lju], [Tom]).

## REFERENCES

- [48Wil] H. Wilsdorf, "The Crystal Structure of the Monovalent Copper Azide  $\text{Cu}_3\text{N}$ ", *Acta Cryst.* 1 (1948) 115-118
- [66Mue] K. Müller and H. Rebsch, "Silicon Nitride - Corrosion Resistant and Stable Against Aluminium", *Silikattechnik* 17 (1966) 279-282
- [66Yas] G. A. Yasinskaya, "The Wetting of Refractory Carbides, Borides and Nitrides by Molten Metals", *Porosh. Met.* (7) (1966) 53-56
- [68Soe] R. Söderquist, "Studies on Explosives. I. The Crystal Structure of Copper(II) Azide, Catena-diazido copper(II)", *Acta Cryst.* 24B (1968) 450-455
- [69Fel] H. Feld, E. Gugel and H. G. Nitzsche, "Silicon Nitride - A Corrosion Resistant High Temperature Material", *Werkstoffe und Korrosion* 20 (1969) 571-574
- [75Lei] G. Leimer and E. Gugel, "Infiltration Composites Based on Silicon Nitride", *Z. Metallk.* 66 (1975) 570-576
- [76Fro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, FRG, 1976)
- [84Bai] A. Baiker und M. Maciejewski, "Formation and Thermal Stability of Copper and Nickel Nitrides", *J. Chem. Soc. Faraday Trans. I* 80 (1984) 2331-2341
- [85Vil] P. Villars and L. D. Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, OH, 1985)
- [86Mas] T. B. Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer. Soc. Met., Metals Park, OH, 1986)
- [87Nak] M. Naka, M. Kubo and I. Okamoto, "Wettability of Silicon Nitride by Aluminium, Copper and Silver", *J. Mater. Sci. Let.* 6 (1987) 965-966
- [89Lju] L. Ljungberg and R. Warren, "Wetting of Silicon Nitride with Reactive Metals and Alloys", *Ceram. Eng. Sci. Proc.* 10 (1989) 1655-1666
- [89Tom] A. P. Tomsia, J. A. Pask, R. E. W. Loemann, "Joining of Nitride Ceramics", *Ceram. Eng. Sci. Proc.* 10 (1989) 1631-1654
- [90Wei] F. Weitzer, K. Remschnig, J. C. Schuster and P. Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M= Al, Cu, Zn, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi)", *J. Mater. Sci.* 5 (1990) 2152-2159

Table 29.1: Solid phases in the system Cu - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Cu	cF4 Fm $\bar{3}$ m Cu (A1)	a= 361.48	[85V11]; powder pattern: ASTM file card # 4-836
$\alpha$ -Cu <sub>3</sub> Si 552<T<842	hP2 P6 <sub>3</sub> /mmc Mg (A3)	a= 255.99 c= 418.49	[85V11]; at 12 at% Si
$\beta$ -Cu <sub>6</sub> Si(h) T>785	cI2 Im3m W (A2)	a= 285.4	[85V11]
$\gamma$ -Cu <sub>5</sub> Si(r) T<729	cP20 P4 <sub>1</sub> 32 $\beta$ Mn (A13)	a= 622.3	[85V11]; powder pattern: ASTM file card # 4-841
$\delta$ -Cu <sub>5</sub> Si(h) (Cu <sub>17</sub> Si <sub>3</sub> ) T>710	t**	a= 881.5 c= 790.3	[85V11]
$\epsilon$ -Cu <sub>15</sub> Si <sub>4</sub> (r) T<800	cI76 I $\bar{4}$ 3d Cu <sub>15</sub> Si <sub>4</sub>	a= 971.4	[85V11]; powder pattern: ASTM file card # 23-222
$\eta$ -Cu <sub>9</sub> Si(h) 558<T<859	hP72	a= 704.5 c= 2195.0	[85V11]
$\eta'$ -Cu <sub>9</sub> Si(h)	hR* R $\bar{3}$	a= 2540 c= 4420	[85V11]
$\eta''$ -Cu <sub>9</sub> Si(r)	t**	a= 726.7 c= 789.2	[85V11]; powder pattern: ASTM file card # 23-224
Cu <sub>3</sub> N	cP4 Pm $\bar{3}$ m ReO <sub>3</sub> (DO <sub>3</sub> )	a= 381.3	[85V11]; powder pattern: ASTM file card # 2-1156

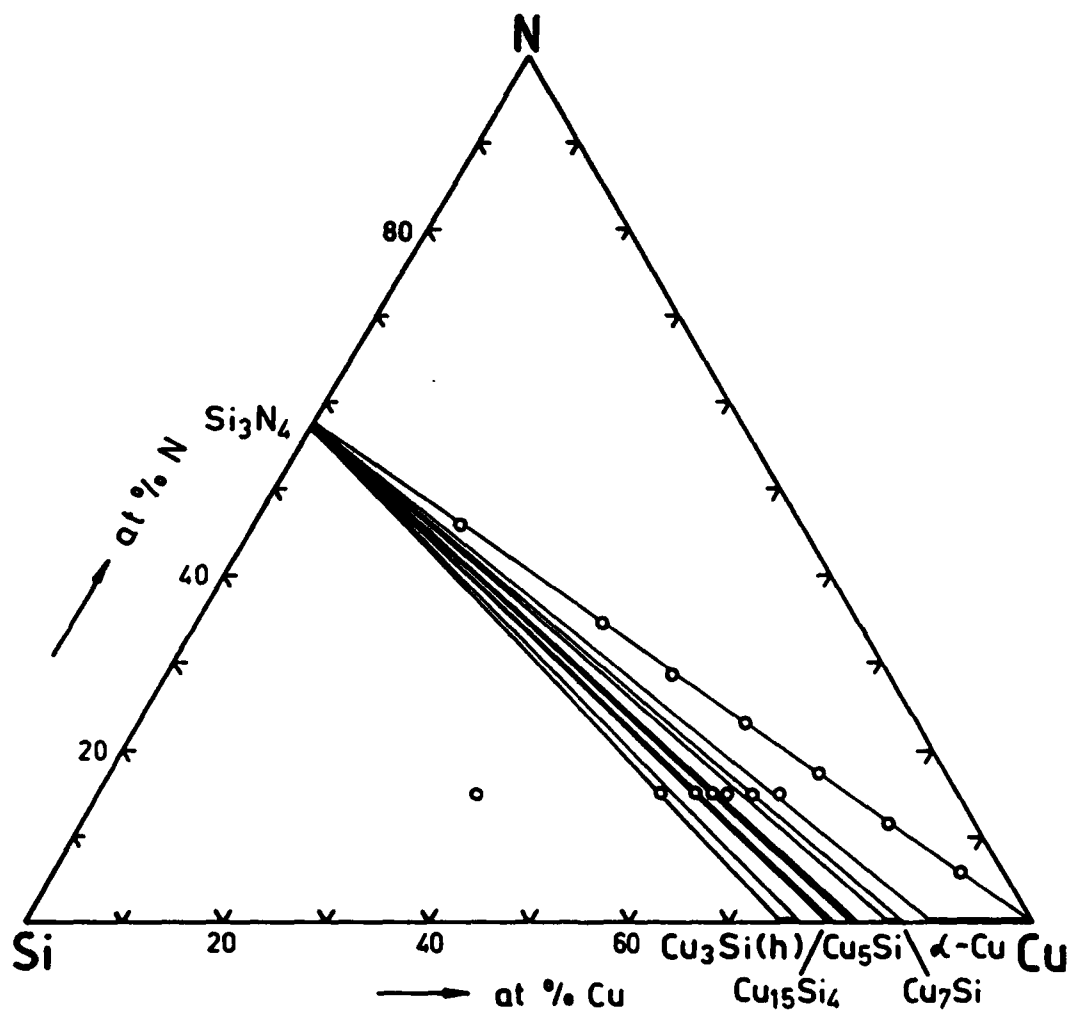


Tab.29.1 continued

CuN <sub>3</sub>	tI32	a= 365.3	[85Vil];powder pattern:
	I4 <sub>1</sub> /a	c= 559.4	ASTM file card # 4-622
CuN <sub>6</sub>	oP28	a= 1348.1	[85Vil];powder pattern:
	Pnma	b= 308.4	ASTM file card # 21-281
		c= 907.6	
Si	cF8	a= 542.86	[85Vil];powder pattern:
	Fd3m		ASTM file card # 5-565
	C (A4)		
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28	a= 781.8	[85Vil];powder pattern:
	P31c	c= 559.1	ASTM file card # 9-250
	Si <sub>3</sub> N <sub>4</sub>		
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14	a= 760.8	[85Vil];powder pattern:
	P6 <sub>3</sub> /m	c= 291.1	ASTM file card # 29-1132
	Si <sub>3</sub> N <sub>4</sub>		33-1160

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Fig.29.1: Isothermal section observed in the system Cu - Si - N  
at 700°C



## SYSTEM SILVER - SILICON - NITROGEN (Ag-Si-N)

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### INTRODUCTION / EXPERIMENTAL

The phase equilibria of Ag-Si-N at 700°C and 900°C were determined by x-ray analysis [90Wei]. The alloys investigated were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si; from Alpha Div., Ventron Corp., USA) and high purity ("puriss") Ag.

### BINARY SYSTEMS

The equilibrium diagram for the simple eutectic (845°C, 10 at% Si) system Ag-Si is given in [86Mas]. Structural data of two metastable Ag-silicides are listed in [85Vil]. No phase diagram exists in the literature for the systems Ag-N and Si-N. In the system Ag-N two intermediate phases are reported (tab.30.1). Neither phase is stable at 700°C or higher temperatures. Silicon nitride exists in two modifications  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.30.1). The solubility of nitrogen in silver as well as in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Ag-Si-N at 700°C or 900°C (tab.30.1). Fig.30.1 shows the isothermal section at 900°C: Ag coexists with  $\text{Si}_3\text{N}_4$  in equilibrium confirming earlier data [66Mue]. Lattice parameter measurements indicate mutual insolubility of Ag and  $\text{Si}_3\text{N}_4$ .

### MISCELLANEOUS

Liquid silver does not wet  $\text{Si}_3\text{N}_4$  [69Fel] ( $\theta = 145 \pm 10^\circ$  under vacuum [66Mue], [87Nak], [89Lju]).

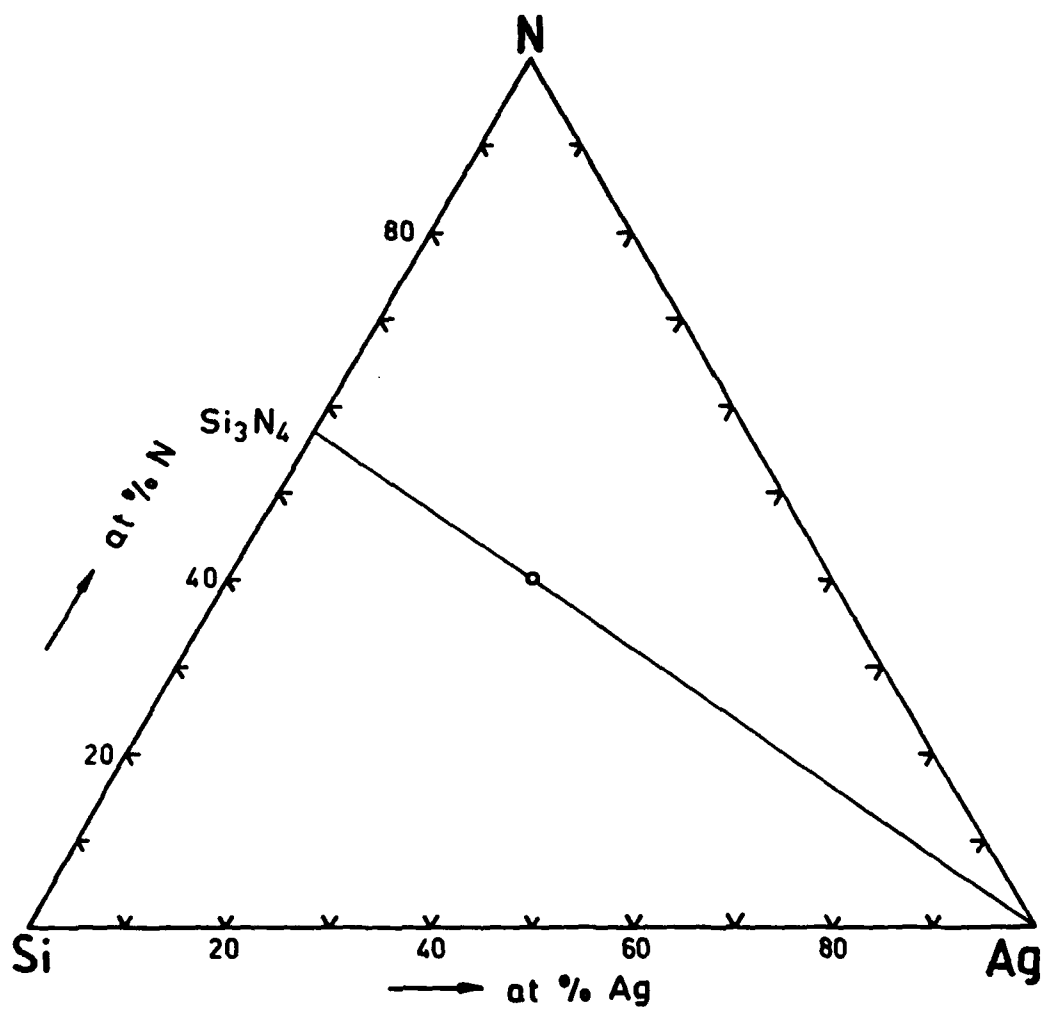
## REFERENCES

- [66Mue] K.Müller and H.Rebsch, "Silicon Nitride - Corrosion Resistant and Stable Against Aluminium", *Silikattechnik* 17 (1966) 279-282
- [69Fel] H.Feld, E.Gugel and H.G.Nitzsche, "Silicon Nitride - A Corrosion Resistant High Temperature Material", *Werkstoffe und Korrosion* 20 (1969) 571-574
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, FRG, 1976)
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [87Nak] M.Naka, M.Kubo and I.Okamoto, "Wettability of Silicon Nitride by Aluminium, Copper and Silver", *J.Mater.Sci.Let.* 6 (1987) 965-966
- [89Lju] L.Ljungberg and R.Warren, "Wetting of Silicon Nitride with Reactive Metals and Alloys", *Ceram.Eng.Sci.Proc.* 10 (1989) 1655-1666
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M= Al, Cu, Zn, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi)", *J.Mater. Sci.* 5 (1990) 2152-2159

Table 30.1: Solid phases in the system Ag - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Ag	cF4 Fm $\bar{3}$ m Cu (A1)	a= 408.53	[85Vil]; powder pattern: ASTM file card # 4-783
Ag <sub>3</sub> N	cF*	a= 437.8	[85Vil]
AgN <sub>3</sub>	oI*	a= 561.7 b= 591.46 c= 600.57	[85Vil]; powder pattern: ASTM file card # 3-906
Si	cF8 Fd $\bar{3}$ m C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160

Fig.30.1 : Isothermal section observed in the system Ag - Si - N  
at 900°C



## SYSTEM GOLD - SILICON - NITROGEN (Au-Si-N)

### INTRODUCTION / EXPERIMENTAL

The phase equilibria of Au-Si-N at 900°C were determined by X-ray analysis [90Wei]. The alloys investigated were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ ; 58 at% Si; from Alpha Div., Ventron Corp., USA) and high purity ("puriss.") Au.

### BINARY SYSTEMS

The equilibrium diagram for the simple eutectic (363°C, 18.6 at% Si) system Au-Si is given in [86Mas]. The existence of several metastable Au-silicides is reported [85Vil], [81Tsa]. No phase diagrams exist in the literature for the systems Au-N and Si-N. In the System Au-N no intermediate phase is reported [84Oka]. Silicon nitride exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.31.1). The solubility of nitrogen in gold [84Oka] as well as in silicon [76Fro] is very low.

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Au-Si-N at 900°C (tab.31.1). Fig.31.1 shows the isothermal section at 900°C : Confirming earlier data [69Fel] Au and  $\text{Si}_3\text{N}_4$  coexist in equilibrium. It should be noted, however, that mechanical stress in thin films of Au deposited on  $\text{Si}_3\text{N}_4$  can cause the formation the metastable phase  $\text{Au}_5\text{Si}_2$  (hex.,  $a=938.2\text{pm}$ ,  $c=1545.9\text{pm}$  [81Tsa]; powder pattern: ASTM file card # 36-938) upon the partial decomposition of  $\text{Si}_3\text{N}_4$  at low nitrogen partial pressure [89Ede]. Lattice parameter measurements indicate mutual insolubility of Au and  $\text{Si}_3\text{N}_4$ .

### MISCELLANEOUS

Gold does not wet silicon nitride ( $\theta = 157^\circ$ ) [89Lju].

## REFERENCES

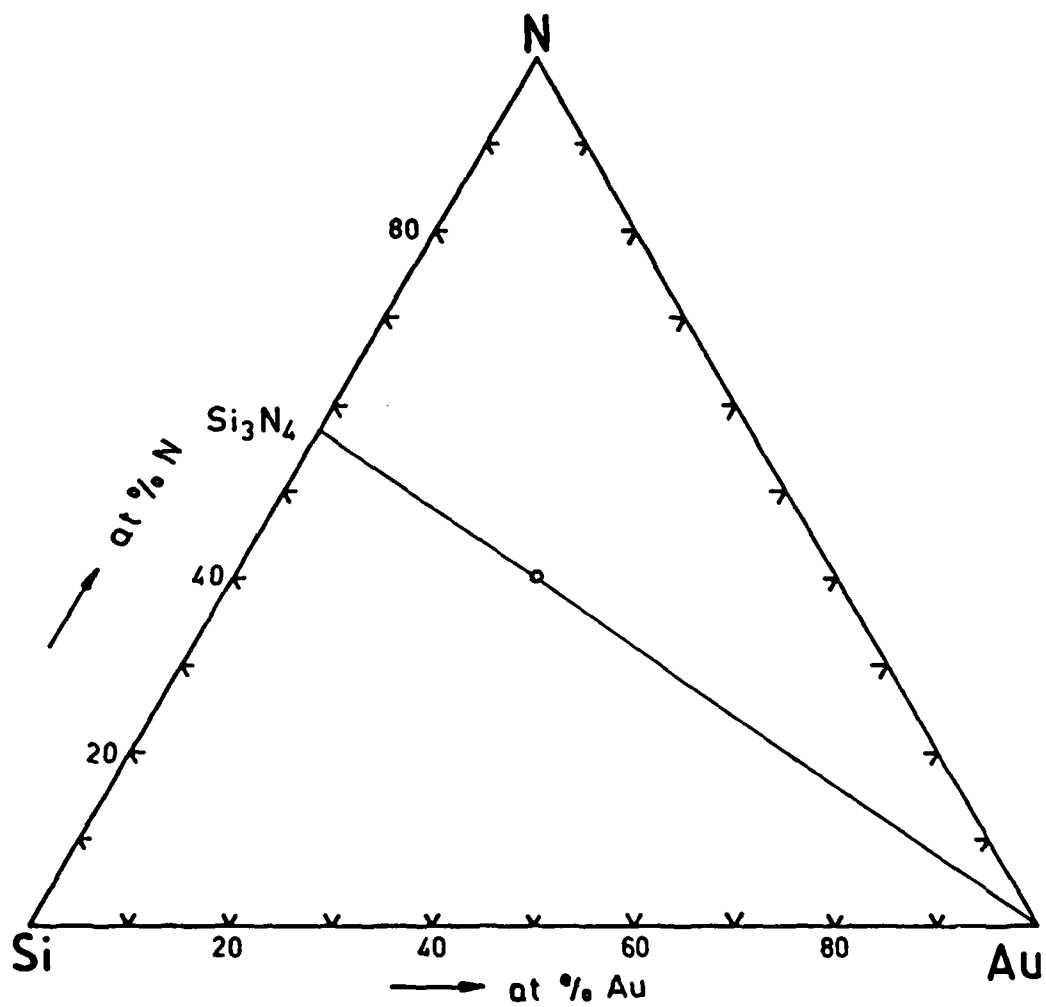
- [69Fel] H.Feld, E.Gugel and H.G.Nitzsche, "Silicon Nitride - A Corrosion Resistant High Temperature Material", *Werkstoffe und Korrosion* 20 (1969) 571-574
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, FRG, 1976)
- [81Tsa] B.Y.Tsaur and J.W.Mayer, "Metastable Au-Si Alloy Formation Induced by Ion Beam Interface Mixing", *Philos.Mag.* A43 (1981) 345-361
- [84Oka] H.Okamoto and T.B.Massalski, "The Au-N (Gold - Nitrogen) System", *Bull.Alloy Phase Diagr.* 5 (1984) 381
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [89Ede] F.Edelman, G.Gutamas and R.Brener, "Interfacial Reactions in the Al/Si<sub>3</sub>N<sub>4</sub>/Si and Au/Si<sub>3</sub>N<sub>4</sub>/Si Systems", paper J3.4, Mater.Res. Soc.Spring Meeting, San Diego, USA, 1989
- [89Lju] L.Ljungberg and R.Warren, "Wetting of Silicon Nitride with Reactive Metals and Alloys", *Ceram.Eng.Sci.Proc.* 10 (1989) 1655-1666
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M= Al, Cu, Zn, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi)", *J.Mater. Sci.* 5 (1990) 2152-2159



Table 31.1: Solid phases at in the system Au - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Au	cF4 Fm $\bar{3}$ m Cu (A1)	a= 407.89	[85V11];powder pattern: ASTM file card # 4-784
Si	cF8 Fd $\bar{3}$ m C (A4)	a= 542.86	[85V11];powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85V11];powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85V11];powder pattern: ASTM file card # 29-1132 33-1160

Fig.31.1: Isothermal section observed in the system Au - Si - N  
at 900°C



## SYSTEM ZINC- SILICON - NITROGEN (Zn-Si-N)

### INTRODUCTION / EXPERIMENTAL

The phase equilibria of Zn-Si-N at 350°C were determined by x-ray analysis [90Wei]. The alloys investigated were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ ; 58 at% Si; from Alpha Div., Ventron Corp., USA) and Zn (m3N+, from Alpha Div., Ventron Corp., USA).

### BINARY SYSTEMS

The phase diagram for the simple eutectic (419.3°C, 0.045 at% Si) system Zn-Si is given in [86Mas]. No Phase diagrams exist in the literature for Zn-N and Si-N. In the system Zn-N the phase  $\text{Zn}_3\text{N}_2$  (tab.32.1) exists up to 700°C [88Wri]. For the azide  $\text{ZnN}_3$ , which decomposes around 300°C [88Wri], two structures are reported (tab.32.1). Silicon nitride exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.32.1). The solubility of nitrogen in zinc [88Wri] as well as in silicon [76Fro] is very low.

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Zn-Si-N at 350°C (tab.32.1). Fig.32.1 shows the isothermal section at 350°C : Confirming earlier data [65Yas], [69Fel] Zn coexists with  $\text{Si}_3\text{N}_4$  in equilibrium. Lattice parameter measurements indicate mutual insolubility of Zn and  $\text{Si}_3\text{N}_4$ .

### MISCELLANEOUS

Liquid zinc does not wet  $\text{Si}_3\text{N}_4$  [66Mue].

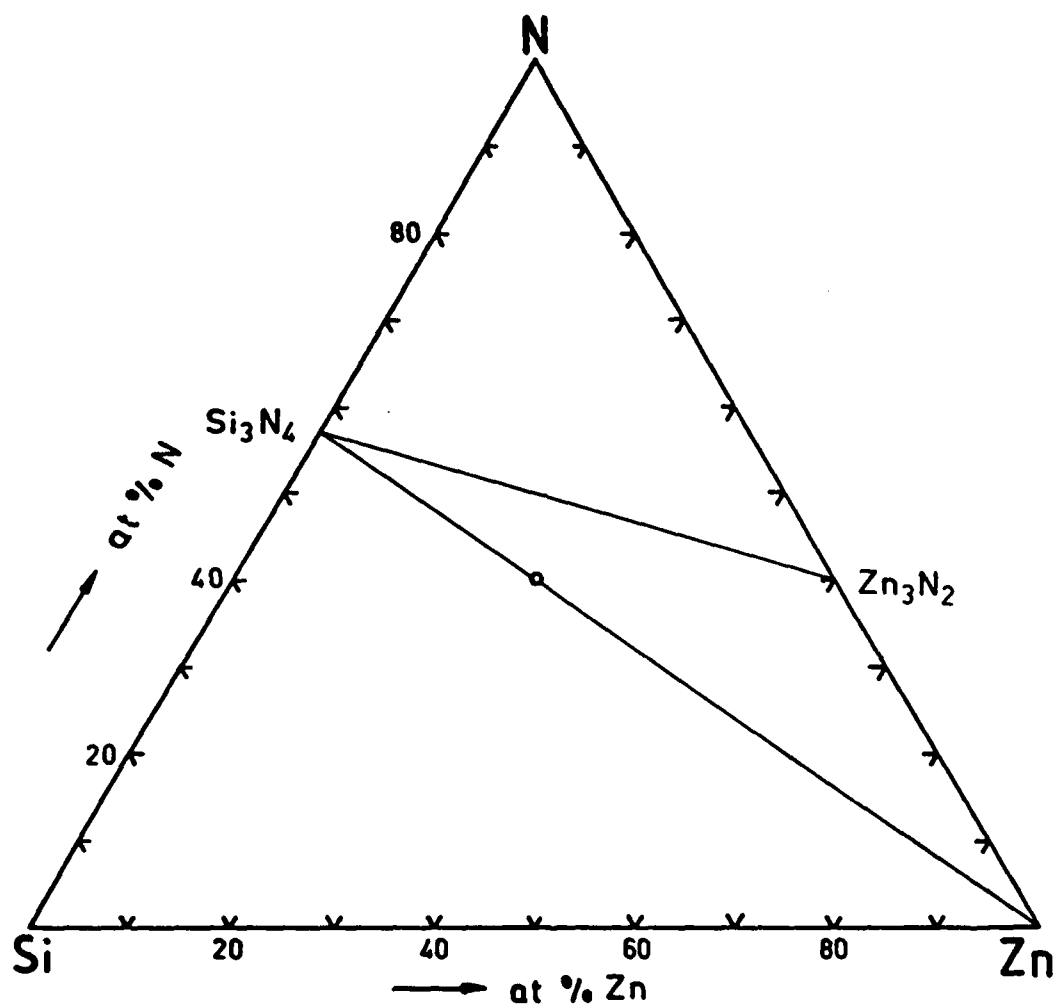
# REFERENCES

- [65Yas] G.A.Yasinskaya, "Reactions of High Melting Compounds with Molten Metals", *Ogneupory* 30 (1965) 20-23
- [66Mue] K.Müller and H.Rebsch, "Silicon Nitride - Corrosion Resistant and Stable Against Aluminium", *Silikattechnik* 17 (1966) 279-282
- [69Fel] H.Feld, E.Gugel and H.G.Nitzsche, "Silicon Nitride - A Corrosion Resistant High Temperature Material", *Werkstoffe und Korrosion* 20 (1969) 571-574
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, FRG, 1976)
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [88Wri] H.A.Wriedt, "The N-Zn (Nitrogen-Zinc) System", *Bull.Alloy Phase Diagr.* 9 (1988) 247-251
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M= Al, Cu, Zn, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi)", *J.Mater. Sci.* 5 (1990) 2152-2159

Table 32.1: Solid phases in the system Zn - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Zn	hP2 P6 <sub>3</sub> /mmc Mg (A3)	a= 266.46 c= 494.61	[85Vil]; powder pattern: ASTM file card # 4-831
Zn <sub>3</sub> N <sub>2</sub>	cI80 Ia $\bar{3}$ Mn <sub>2</sub> O <sub>3</sub> (D <sub>5h</sub> )	a= 976.3	[85Vil]; powder pattern: ASTM file card # 35-762
$\alpha$ -ZnN <sub>6</sub>	oP36 P222 <sub>1</sub>	a= 1098 b= 692 c= 1633	[85Vil]; powder pattern: ASTM file card # 30-1473
$\beta$ -ZnN <sub>6</sub>	o*28	a= 735 b= 437 c= 1523	[88Wri]; powder pattern: ASTM file card # 23-740
Si	cF8 Fd $\bar{3}m$ C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160

Fig.32.1 : Isothermal section observed in the system Zn - Si - N  
at 350°C



## SYSTEM CADMIUM - SILICON - NITROGEN (Cd-Si-N)

### INTRODUCTION / EXPERIMENTAL

The phase equilibria of Cd-Si-N at 300°C were determined by X-ray analysis [90Wei]. The alloys investigated were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ ; 58 at% Si; from Alpha Div., Ventron Corp., USA) and Cd (3N, from Alpha Div., Ventron Corp., USA).

### BINARY SYSTEMS

The phase diagram for the simple eutectic (320°C, 0.135 at% Si) system Cd-Si is given in [86Mas]. No phase diagram exists in the literature for Cd-N and Si-N. The nitride  $\text{Cd}_3\text{N}_2$  (tab.33.1) decomposes at 180°C in an atmosphere of  $\text{NH}_3$  (pressure not specified) [88Wri]. The azide  $\text{CdN}_3$  decomposes around 100°C [88Wri]. Silicon nitride exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.33.1). The solubility of nitrogen in cadmium [88Wri] as well as in silicon [76Fro] is very low.

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Cd-Si-N at 300°C (tab.33.1). Fig.33.1 shows the isothermal section at 300°C: Confirming earlier data [65Yas], [69Fel] Cd coexists with  $\text{Si}_3\text{N}_4$  in equilibrium. Lattice parameter measurements indicate mutual insolubility of Cd and  $\text{Si}_3\text{N}_4$ .

### MISCELLANEOUS

Liquid cadmium does not wet  $\text{Si}_3\text{N}_4$  ( $\theta = 157^\circ$  under vacuum [66Mue]).

## REFERENCES

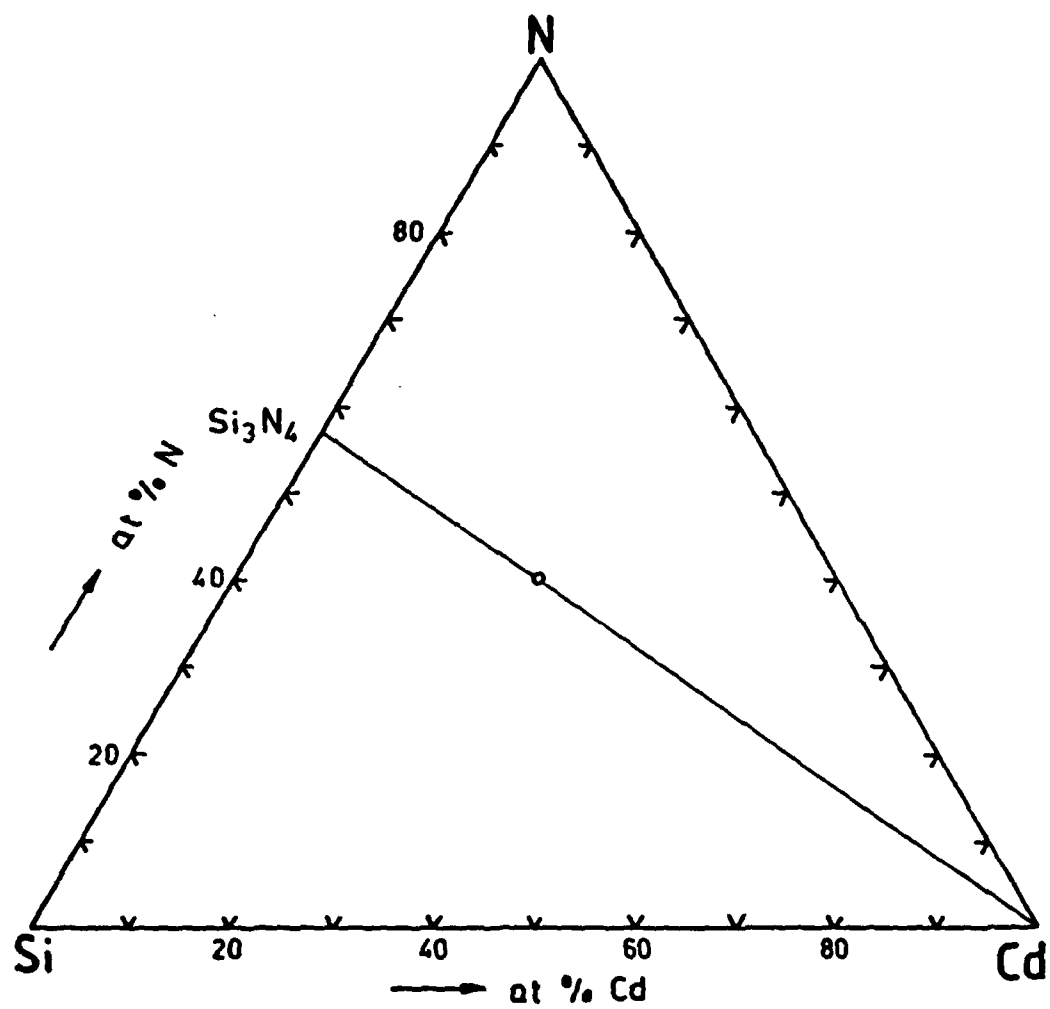
- [65Yas] G.A.Yasinskaya, "Reactions of High Melting Compounds with Molten Metals", *Ogneupory* 30 (1965) 20-23
- [66Mue] K.Müller and H.Rebsch, "Silicon Nitride - Corrosion Resistant and Stable Against Aluminium", *Silikattechnik* 17 (1966) 279-282
- [69Fel] H.Feld, E.Gugel and H.G.Nitzsche, "Silicon Nitride - A Corrosion Resistant High Temperature Material", *Werkstoffe und Korrosion* 20 (1969) 571-574
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, FRG, 1976)
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [88Wri] H.A.Wriedt, "The Cd-N (Cadmium-Nitrogen) System", *Bull.Alloy Phase Diagr.* 9 (1988) 245-247
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M= Al, Cu, Zn, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi)", *J.Mater. Sci.* 5 (1990) 2152-2159



Table 33.1: Solid phases in the system Cd - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space Group / Prototype	Lattice Parameters (pm)	Comments
Cd	hP2 P6 <sub>3</sub> /mmc Mg (A3)	a= 297.87 c= 561.66	[85Vil]; powder pattern: ASTM file card # 5-674
Cd <sub>3</sub> N <sub>2</sub>	cI80 Ia $\bar{3}$ Mn <sub>2</sub> O <sub>3</sub> (D5 <sub>h</sub> )	a= 1081	[85Vil]; powder pattern: ASTM file card # 10-253
CdN <sub>6</sub>	oP56 Pbca	a= 782 b= 646 c= 1604	[85Vil]
Si	cF8 Fd $\bar{3}$ m C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160

Fig.33.1 : Isothermal section observed in the system Cd - Si - N  
at 300°C



## SYSTEM ALUMINIUM - SILICON - NITROGEN (Al-Si-N)

### INTRODUCTION / EXPERIMENTAL

The phase equilibria of Al-Si-N at 600°C were investigated by x-ray analysis [90Wei], transmission electron microscopy (TEM) and Auger electron spectroscopy (AES) [89Bre]. The alloys investigated in [90Wei] were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si, from Alpha Div., Ventron Corp., USA), AlN (2N, from Koch Light Lab. Ltd., UK), silicon (m4N, from Fluka AG, Switzerland) and aluminium (2N8, from Koch Light Lab. Ltd., UK).

### BINARY SYSTEMS

The phase diagrams for the systems Al-Si as well as Al-N are given in [86Mas]. AlN is the only stable intermediate phase (tab.34.1). No phase diagram is reported for Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.34.1). The solubility of nitrogen in aluminium as well as in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Al-Si-N (tab.34.1). Fig.34.1 shows the isothermal section at 600°C in the absence of external nitrogen pressure. Although expected from thermochemical data [76Fro], x-ray data of samples prepared from Al +  $\text{Si}_3\text{N}_4$  did not show the formation of Si + AlN. However, the occurrence of this reaction was observed by AES [89Bre] and TEM [86Nak] [89Bre]: Around each grain of Al a thin layer of AlN is formed acting as a diffusion barrier and retarding further progress of the reaction. Thus the phases observed by x-ray (fig.34.1) coexist in metastable equilibrium even after anneal for several hundred hours.

## MISCELLANEOUS

The wetting angle of liquid aluminium on  $\text{Si}_3\text{N}_4$  is found to be  $\theta = 126^\circ$  [66Mue],[66Yas],[87Nak]. However at temperatures above  $1100^\circ\text{C}$  Al wets  $\text{Si}_3\text{N}_4$  ( $\theta = 72^\circ$ ) [89Lju],[89Tom].

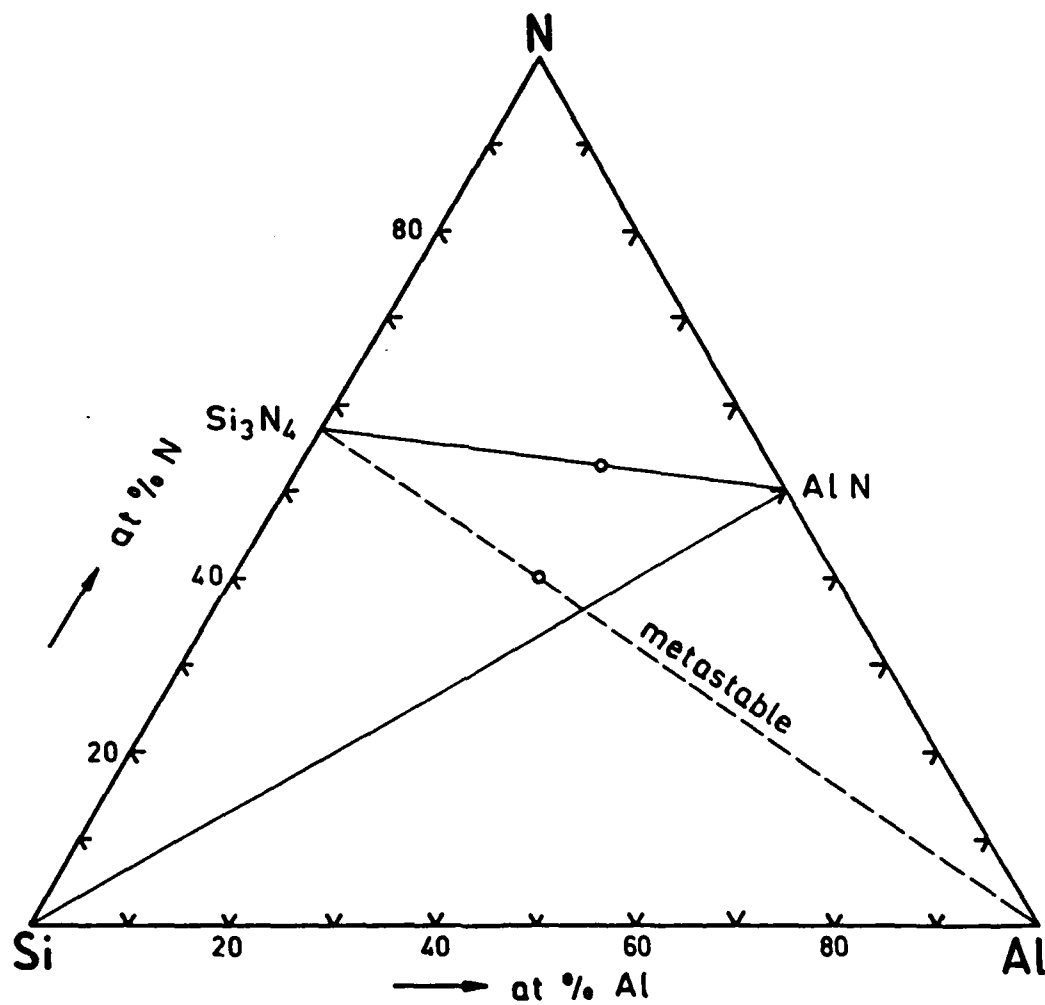
## REFERENCES

- [66Mue] K.Müller and H.Rebsch, "Silicon Nitride - Corrosion Resistant and Stable Against Aluminium", *Silikattechnik* 17 (1966) 279-282
- [66Yas] G.A.Yasinskaya, "The Wetting of Refractory Carbides, Borides and Nitrides by Molten Metals", *Porosh.Met.* (7) (1966) 53-56
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [86Nak] M.Naka, H.Mori, M.Kubo, I.Okamoto and H.Fujita, "Observation of Al/ $\text{Si}_3\text{N}_4$  Interface", *J.Mater.Sci.Lett.* 5 (1986) 696-698
- [87Nak] M.Naka, M.Kubo and I.Okamoto, "Wettability of Silicon Nitride by Aluminium, Copper and Silver", *J.Mater.Sci.Lett.* 6 (1987) 965-966
- [89Bre] R.Brener, F.Edelman and E.Y.Gutamas, "Formation of an Interfacial AlN Layer in an Al/ $\text{Si}_3\text{N}_4$  Thin Film System", *Appl.Phys.Lett.* 54 (1989) 901-903
- [89Lju] L.Ljungberg and R.Warren, "Wetting of Silicon Nitride with Reactive Metals and Alloys", *Ceram.Eng.Sci.Proc.* 10 (1989) 1655-1666
- [89Tom] A.P.Tomsia, J.A.Pask, R.EW.Loemann, "Joining of Nitride Ceramics", *Ceram.Eng.Sci.Proc.* 10 (1989) 1631-1654
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M= Al, Cu, Zn, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi)", *J.Mater. Sci.* 5 (1990) 2152-2159

Table 34.1: Solid phases in the system Al - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Al	cF4 Fm $\bar{3}$ m Cu (Al)	a= 404.88	[85Vil]; powder pattern: ASTM file card # 4-787
AlN	hP4 P6 <sub>3</sub> mc SZn (B4)	a= 311.0 c= 498.0	[85Vil]; powder pattern: ASTM file card # 25-1133
Si	cF8 Fd $\bar{3}$ m C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160

**Fig.34.1: Isothermal section observed in the system Al - Si - N  
at 600°C**



## SYSTEM INDIUM - SILICON - NITROGEN (In-Si-N)

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### INTRODUCTION / EXPERIMENTAL

The phase equilibria of In-Si-N at 120°C were determined by x-ray analysis [90Wei]. The alloys investigated in this work were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si, from Alpha Div., Ventron Corp., USA) and indium (4N, from Fluka AG, Switzerland).

### BINARY SYSTEMS

The phase diagrams for the system In-Si is given in [86Mas]. No phase diagrams are reported for In-N or Si-N. The phase InN (tab.35.1) decomposes at 680°C under  $10^5$  Pa  $\text{N}_2$  [38Juz], [87Jon].  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.35.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHEPMAL SECTIONS

No ternary phase is observed in In-Si-N (tab.35.1). Fig.35.1 shows the isothermal section at 120°C in the absence of external nitrogen pressure. In agreement with thermochemical data [76Fro] indium coexists with  $\text{Si}_3\text{N}_4$  in equilibrium. Lattice parameter measurements indicate mutual insolubility of In and  $\text{Si}_3\text{N}_4$ .

### MISCELLANEOUS

Indium does not wet silicon nitride [89Lju], [90oe].

### REFERENCES

- [38Juz] R. Juza and H. Hahn, "On the Crystal Structures of  $\text{Cu}_3\text{N}$ , GaN and InN", *Z. Anorg. Allg. Chem.* **239** (1938) 282-287
- [76Fro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [85Vil] P. Villars and L. D. Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, OH., 1985)
- [86Mas] T. B. Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer. Soc. Met., Metals Park, OH., 1986)

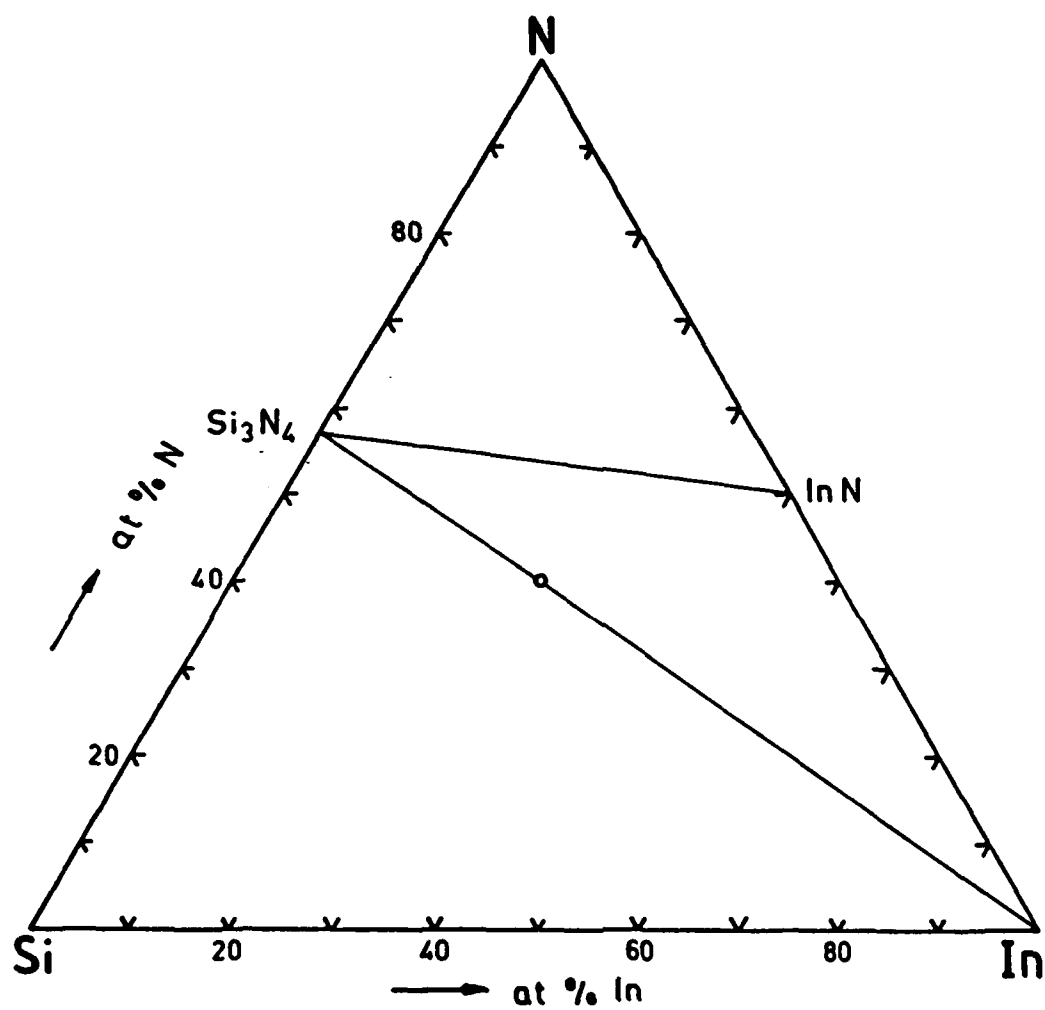
- [87Jon] R.D.Jones and K.Rose, "Thermal Stability of InN", J.Phys.Chem. Solids 48 (1987) 587-590
- [89Lju] L.Ljungberg and R.Warren, "Wetting of Silicon Nitride with Reactive Metals and Alloys", Ceram.Eng.Sci.Proc.10 (1989) 1655-1666
- [90Loe] R.E.Loemann, A.P.Tomsia, J.A.Pask and S.M.Johnson, "Bonding Mechanisms in Silicon Nitride Brazing", J.Amer.Ceram.Soc. 73 (1990) 552-558
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M= Al, Cu, Zn, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi)", J.Mater. Sci.5 (1990) 2152-2159

Table 35.1: Solid phases in the system In - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
In	tI2 F4/mmm In (A6)	a= 325.12 c= 494.67	[85Vil]; powder pattern: ASTM file card # 5-642
InN	hP4 P6 <sub>3</sub> /mc SZn (B4)	a= 354.0 c= 570.4	[85Vil]; powder pattern: ASTM file card # 2-1450
Si	cF8 Fd3m C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160



Fig.35.1: Isothermal section observed in the system In - Si - N  
at 120°C



## SYSTEM THALLIUM - SILICON - NITROGEN (Tl-Si-N)

### INTRODUCTION / EXPERIMENTAL

The phase equilibria of Tl-Si-N at 200°C were determined by x-ray analysis [90Wei]. The alloys investigated in this work were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si, from Alpha Div., Ventron Corp., USA) and thallium (4N, from Fluka AG, Switzerland).

### BINARY SYSTEMS

The phase diagrams for the system Tl-Si is given in [86Mas]. No phase diagrams exist in the literature for Tl-N or Si-N. The nitride TlN is reported (tab.36.1) without further specification of its stability with regard to temperature and nitrogen pressure. The azide  $\text{TlN}_3$  exists at least up to 225°C [73Mau].  $\text{Si}_3\text{N}_4$  occurs in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.36.1). The solubility of nitrogen in silicon as well as in thallium is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Tl-Si-N (tab.36.1). Fig.36.1 shows the isothermal section at 200°C in the absence of external nitrogen pressure: Tl coexists with  $\text{Si}_3\text{N}_4$  in equilibrium. Lattice parameter measurements indicate mutual insolubility of Tl and  $\text{Si}_3\text{N}_4$ .

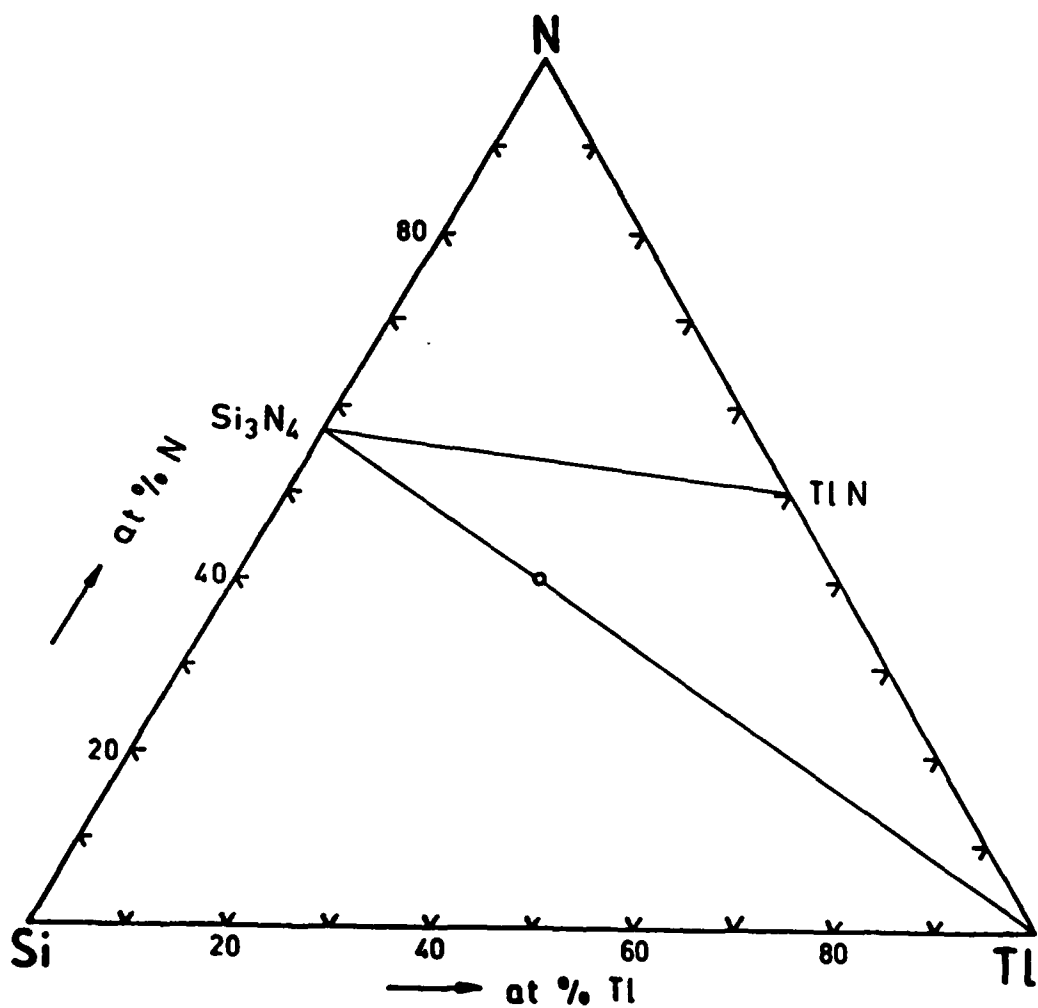
### REFERENCES

- [73Mau] F.A.Mauer, C.R.Hubbard and T.A.Hahn, "Thermal Expansion and Low Temperature Phase Transition of Thallous Azide", J.Chem.Phys. **59** (1973) 3770-3776
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M= Al, Cu, Zn, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi)", J.Mater. Sci. **5** (1990) 2152-2159

Table 36.1: Solid phases in the system Tl - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\alpha$ -Tl(r) T<234°C	hP2 P6 <sub>3</sub> /mmc Mg (A3)	a= 345.66 c= 552.48	[85V11]; powder pattern: ASTM file card # 30-1341
$\beta$ -Tl(h) T>234°C	cI2 Im3m W (A2)	a= 387.1	[85V11]; powder pattern: ASTM file card # 2-876
TlN	hP4 P6 <sub>3</sub> mc SZn (B4)	a= 368 c= 601	[85V11]
TlN <sub>3</sub> (h=r) -25<T<225+	tI16 I4/mcm	a= 620.8 c= 735.5	[85V11]; powder pattern: ASTM file card # 21-1209
Si	cF8 Fd3m C (A4)	a= 542.86	[85V11]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85V11]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85V11]; powder pattern: ASTM file card # 29-1132 33-1160

Fig.36.1: Isothermal section observed in the system Tl - Si - N  
at 200°C



## **SYSTEM TIN - SILICON - NITROGEN (Sn-Si-N)**

### **INTRODUCTION / EXPERIMENTAL**

The phase equilibria of Sn-Si-N at 200°C were determined by x-ray analysis [90Wei]. The alloys investigated in this work were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si, from Alpha Div., Ventron Corp., USA) and tin (5N, from Alpha Div., Ventron Corp., USA).

### **BINARY SYSTEMS**

The phase diagrams for the system Si-Sn is given in [86Mas]. No phase diagrams exist in the literature for Sn-N or Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.37.1). The solubility of nitrogen in silicon as well as in tin is very low [76Fro].

### **SOLID PHASES / ISOTHERMAL SECTIONS**

No ternary phase is observed in Sn-Si-N (tab.37.1). Fig.37.1 shows the isothermal section at 200°C in the absence of external nitrogen pressure: Sn coexists with  $\text{Si}_3\text{N}_4$  in equilibrium. This agrees with earlier literature [65Yas], [69Fel]. Lattice parameter measurements indicate mutual insolubility of tin and  $\text{Si}_3\text{N}_4$ .

### **MISCELLANEOUS**

The wetting angle of liquid tin on  $\text{Si}_3\text{N}_4$  is reported to be  $\theta = 155 \pm 15^\circ$  [66Mue], [89Lju], [89Tom], [90Loe].

### **REFERENCES**

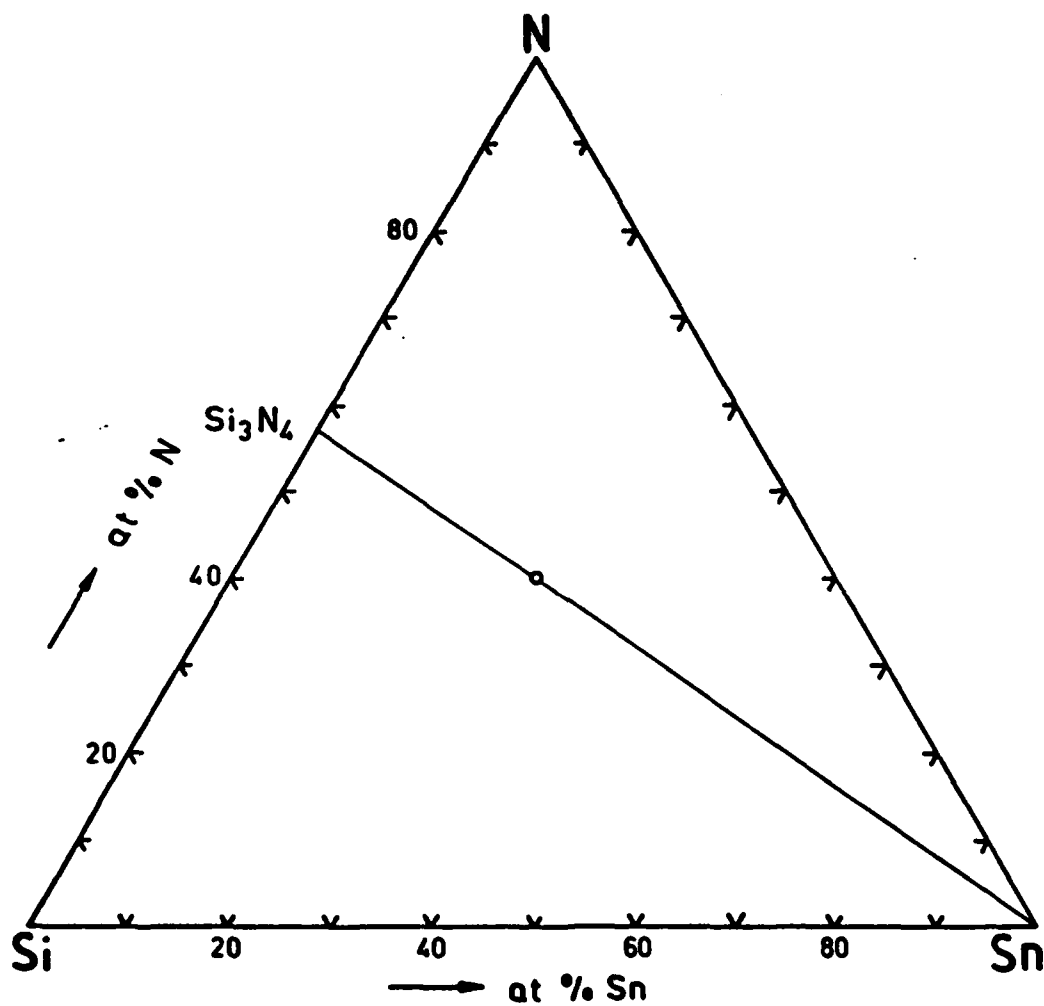
- [65Yas] G.A.Yasinskaya, "Reactions of High Melting Compounds with Molten Metals", *Ogneupory* 30 (1965) 20-23
- [66Mue] K.Müller and H.Rebsch, "Silicon Nitride - Corrosion Resistant and Stable Against Aluminium", *Silikattechnik* 17 (1966) 279-282
- [69Fel] H.Feld, E.Gugel and H.G.Nitzsche, "Silicon Nitride - A Corrosion Resistant High Temperature Material", *Werkstoffe Korros.* 20 (1969) 571-574

- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [89Lju] L.Ljungberg and R.Warren, "Wetting of Silicon Nitride with Reactive Metals and Alloys", Ceram.Eng.Sci.Proc.10 (1989) 1655-1666
- [89Tom] A.P.Tomsia, J.A.Pask, R.EW.Loemann, "Joining of Nitride Ceramics", Ceram.Eng.Sci.Proc.10 (1989) 1631-1654
- [90Loe] R.E.Loemann, A.P.Tomsia, J.A.Pask and S.M.Johnson, "Bonding Mechanisms in Silicon Nitride Brazing", J.Amer.Ceram.Soc. 73 (1990) 552-558
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M= Al, Cu, Zn, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi)", J.Mater. Sci.5 (1990) 2152-2159

Table 37.1: Solid phases in the system Sn - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
$\beta$ -Sn T>13°C	tI4 I4 <sub>1</sub> /amd $\beta$ -Sn (A5)	a= 583.15 c= 318.14	[85Vil]; powder pattern: ASTM file card # 4-673
Si	cF8 Fd $\bar{3}$ m C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160

Fig.37.1: Isothermal section observed in the system Sn - Si - N  
at 200°C



## SYSTEM LEAD - SILICON - NITROGEN (Pb-Si-N)

### INTRODUCTION / EXPERIMENTAL

The phase equilibria of Pb-Si-N at 200°C were determined by x-ray analysis [90Wei]. The alloys investigated in this work were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si, from Alpha Div., Ventron Corp., USA) and lead (2N8, from Alpha Div., Ventron Corp., USA).

### BINARY SYSTEMS

The phase diagrams for the system Pb-Si is given in [86Mas]. No phase diagrams exist in the literature for Pb-N or Si-N. The azide  $\text{PbN}_3$  (tab.38.1) decomposes upon aging at room temperature as well as upon heating to 128°C.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.38.1). The solubility of nitrogen in silicon as well as in lead is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Pb-Si-N (tab.38.1). Fig.38.1 shows the isothermal section at 200°C in the absence of external nitrogen pressure: Pb coexists with  $\text{Si}_3\text{N}_4$  in equilibrium. This agrees with earlier literature [60Coo], [65Yas], [69Fel], [77Ash]. Lattice parameter measurements indicate mutual insolubility of lead and  $\text{Si}_3\text{N}_4$ .

### MISCELLANEOUS

The wetting angle of liquid lead on  $\text{Si}_3\text{N}_4$  is reported to be  $\theta = 159^\circ$  [66Mue].

### REFERENCES

- [60Coo] W.H.Cook, "Corrosion Resistance of Various Ceramics and Cermets to Liquid Metals", US Atomic Energy Comm., ORNL-2391 (1960)
- [65Yas] G.A.Yasinskaya, "Reactions of High Melting Compounds with Molten Metals", *Ogneupory* 30 (1965) 20-23
- [66Mue] K.Müller and H.Rebsch, "Silicon Nitride - Corrosion Resistant and Stable Against Aluminium", *Silikattechnik* 17 (1966) 279-282

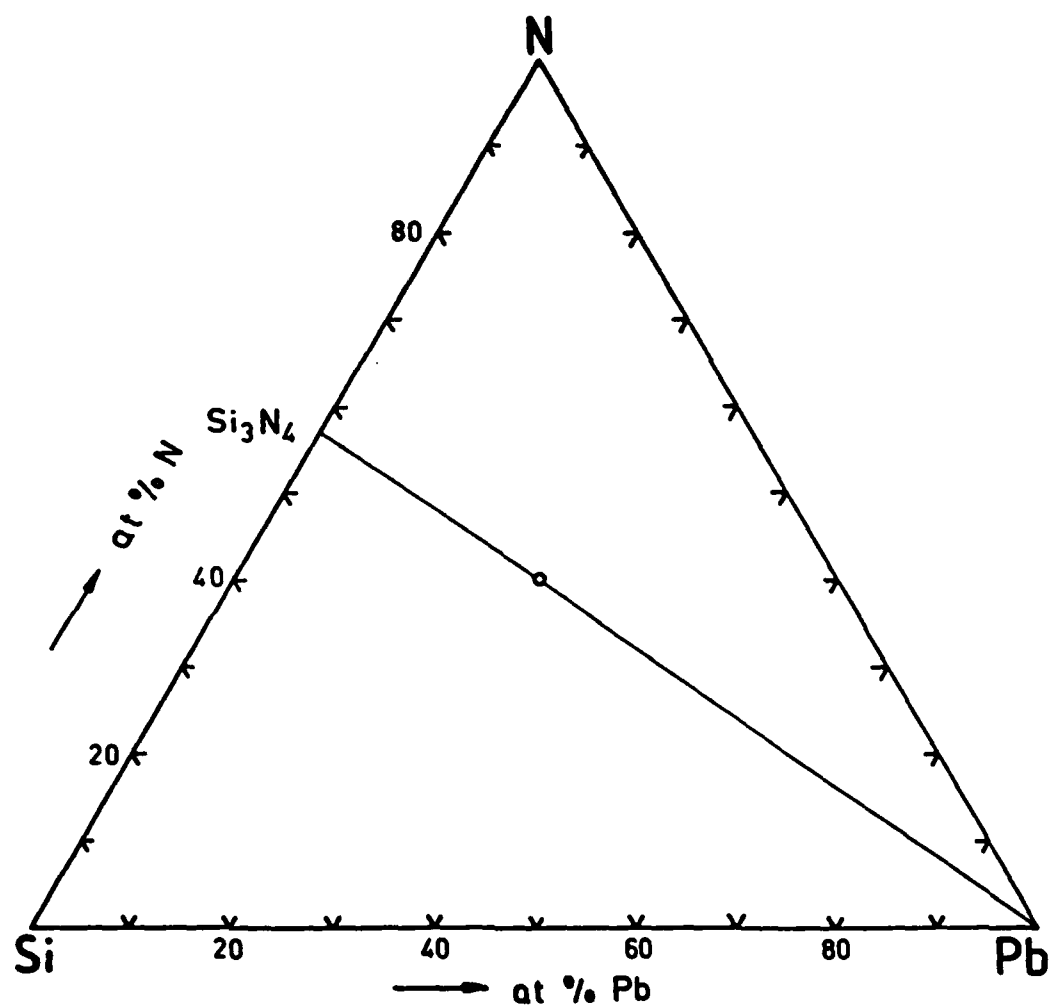


- [69Fel] H.Feld, E.Gugel and H.G.Nitzsche, "Silicon Nitride - A Corrosion Resistant High Temperature Material", *Werkstoffe Korros.* 20 (1969) 571-574
- [76Fro] E.Fromm and E.Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [77Ash] R.C.Asher, D.Davies and S.A.Beetham, "Some Observations on the Compatibility of Structural Materials with Molten Lead", *Corros.Science* 17 (1977) 545-557
- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M= Al, Cu, Zn, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi)", *J.Mater. Sci.* 5 (1990) 2152-2159

Table 38.1: Solid phases in the system Pb - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Pb	CF4 Fm $\bar{3}$ m Cu (A1)	a= 495.07	[85Vil]; powder pattern: ASTM file card # 4-686
PbN <sub>6</sub>	oP84 Pnma	a= 663 b= 1625 c= 1131	[85Vil]; powder pattern: ASTM file card # 14-629 24-82
Si	CF8 Fd $\bar{3}$ m C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160

Fig.38.1: Isothermal section observed in the system Pb - Si - N  
at 200°C



## SYSTEM ANTIMONY - SILICON - NITROGEN (Sb-Si-N)

### INTRODUCTION / EXPERIMENTAL

The phase equilibria of Sb-Si-N at 600°C were determined by x-ray analysis [90Wei]. The alloys investigated in this work were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si, from Alpha Div., Ventron Corp., USA) and antimony (4N, from Fluka AG., Switzerland).

### BINARY SYSTEMS

The phase diagrams for the system Sb-Si is given in [86Mas]. No phase diagrams exist in the literature for Sb-N or Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab.39.1). The solubility of nitrogen in silicon is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Sb-Si-N (tab.39.1). Fig.39.1 shows the isothermal section at 600°C in the absence of external nitrogen pressure: Sb coexists with  $\text{Si}_3\text{N}_4$  in equilibrium. This agrees with earlier literature [88Ahn]. Lattice parameter measurements indicate mutual insolubility of antimony and  $\text{Si}_3\text{N}_4$ .

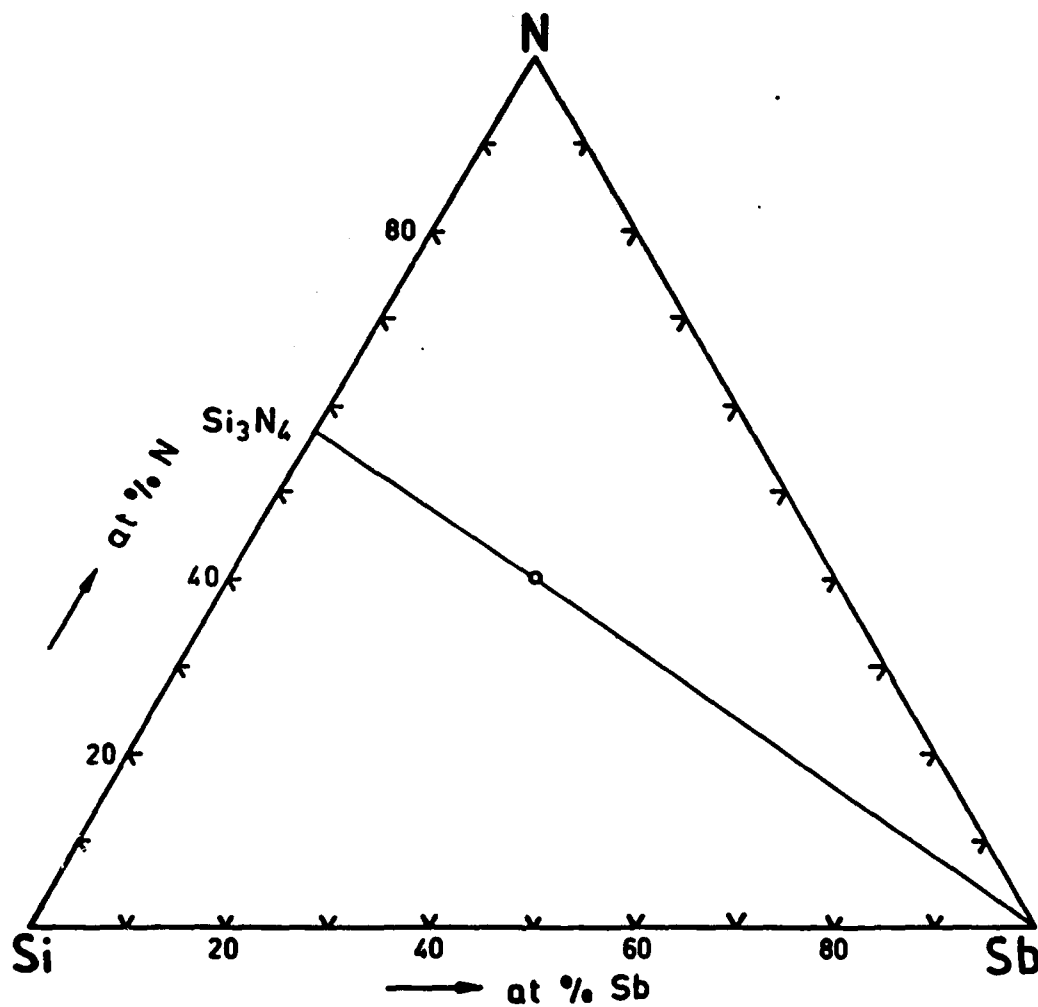
### REFERENCES

- [76Fro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)
- [85Vil] P. Villars and L.D. Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer. Soc. Met., Metals Park, OH., 1985)
- [86Mas] T.B. Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer. Soc. Met., Metals Park, OH., 1986)
- [88Ahn] S.T. Ahn, H.W. Kennel, J.D. Plummer and W.A. Tiller, "Enhanced Sb Diffusion in Si under Thermal  $\text{Si}_3\text{N}_4$  Films during Annealing in Ar", Appl. Phys. Lett. **53** (1988) 1593-1595
- [90Wei] F. Weitzer, K. Remschnig, J.C. Schuster and P. Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M = Al, Cu, Zn, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi)", J. Mater. Sci. **5** (1990) 2152-2159

Table 39.1: Solid phases in the system Sb - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Sb	hR2 R $\bar{3}$ m $\alpha$ -As (A7)	a= 430.84 c= 1127.4	[85Vil]; powder pattern: ASTM file card # 35-732
Si	cF8 Fd $\bar{3}$ m C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 P6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160

Fig.39.1: Isothermal section observed in the system Sb - Si - N  
at 600°C



## SYSTEM BISMUTH - SILICON - NITROGEN (Bi-Si-N)

### INTRODUCTION / EXPERIMENTAL

The phase equilibria of Bi-Si-N at 200°C were determined by x-ray analysis [90Wei]. The alloys investigated in this work were prepared by annealing in evacuated quartz tubes cold pressed powder mixtures of  $\text{Si}_3\text{N}_4$  (mixture of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , 58 at% Si, from Alpha Div., Ventron Corp., USA) and bismuth (3N, from E. Merck, FRG).

### BINARY SYSTEMS

The phase diagrams for the system Bi-Si is given in [86Mas]. No phase diagrams exist in the literature for Bi-N or Si-N.  $\text{Si}_3\text{N}_4$  exists in two modifications:  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  (tab. 40.1). The solubility of nitrogen in silicon as well as in bismuth is very low [76Fro].

### SOLID PHASES / ISOTHERMAL SECTIONS

No ternary phase is observed in Bi-Si-N (tab. 40.1). Fig. 40.1 shows the isothermal section at 200°C in the absence of external nitrogen pressure: Bi coexists with  $\text{Si}_3\text{N}_4$  in equilibrium. This agrees with earlier literature [69Fel]. Lattice parameter measurements indicate mutual insolubility of bismuth and  $\text{Si}_3\text{N}_4$ .

### MISCELLANEOUS

The wetting angle of liquid bismuth on  $\text{Si}_3\text{N}_4$  is reported to be  $\theta > 90^\circ$  (non wetting) [65Yas].

### REFERENCES

- [65Yas] G.A. Yasinskaya, "Reactions of High Melting Compounds with Molten Metals", *Ogneupory* 30 (1965) 20-23
- [69Fel] H. Feld, E. Gugel and H.G. Nitzsche, "Silicon Nitride - A Corrosion Resistant High Temperature Material", *Werkstoffe Korros.* 20 (1969) 571-574
- [76Fro] E. Fromm and E. Gebhardt, "Gase und Kohlenstoff in Metallen" (Springer, Berlin, 1976)

- [85Vil] P.Villars and L.D.Calvert, "Pearsons Handbook of Crystallographic Data for Intermetallic Phases" (Amer.Soc.Met., Metals Park, OH., 1985)
- [86Mas] T.B.Massalski (ed.), "Binary Alloy Phase Diagrams" (Amer.Soc. Met., Metals Park, OH., 1986)
- [90Wei] F.Weitzer, K.Remschnig, J.C.Schuster and P.Rogl, "Phase Equilibria and Structural Chemistry in the Ternary Systems M-Si-N and M-B-N (M= Al, Cu, Zn, Ag, Cd, In, Sn, Sb, Au, Tl, Pb, Bi)", J.Mater. Sci.5 (1990) 2152-2159

Table 40.1: Solid phases in the system Bi - Si - N

Phase / Temperature Range (°C)	Pearson Symbol/ Space group / Prototype	Lattice Parameters (pm)	Comments
Bi	hR2 R $\bar{3}$ m $\alpha$ -As (A7)	a= 454.60 c= 1186.2	[85Vil]; powder pattern: ASTM file card # 5-519
Si	cF8 Fd $\bar{3}$ m C (A4)	a= 542.86	[85Vil]; powder pattern: ASTM file card # 5-565
$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hP28 P31c Si <sub>3</sub> N <sub>4</sub>	a= 781.8 c= 559.1	[85Vil]; powder pattern: ASTM file card # 9-250
$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hP14 F6 <sub>3</sub> /m Si <sub>3</sub> N <sub>4</sub>	a= 760.8 c= 291.1	[85Vil]; powder pattern: ASTM file card # 29-1132 33-1160

Fig.40.1: Isothermal section observed in the system Bi - Si - N  
at 200°C

